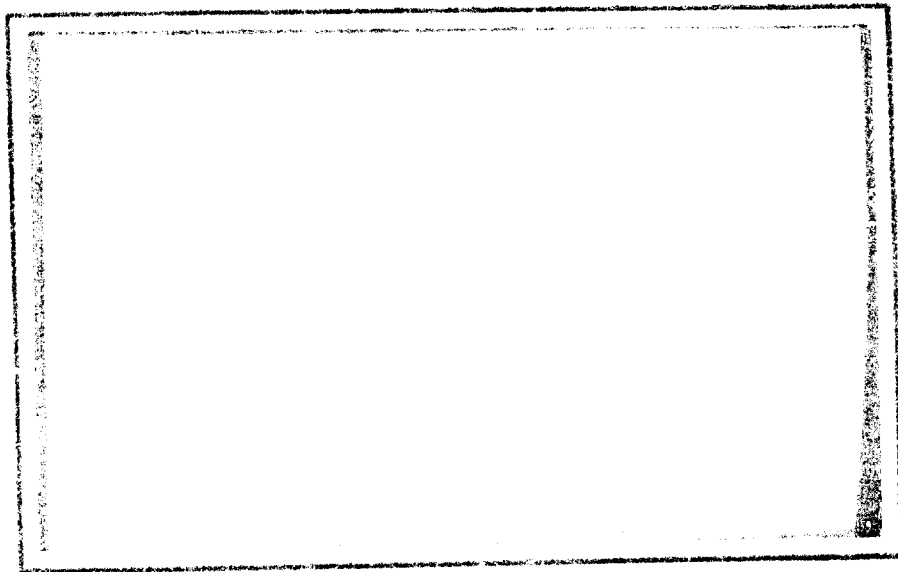


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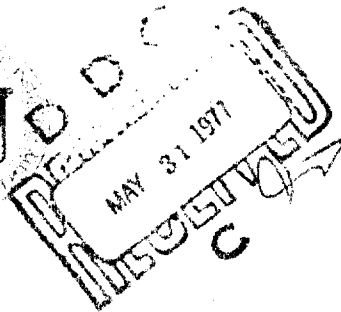
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⑥ KINETICS, ENERGETICS AND INFRARED LASING IN HIGH
ENERGY ROCKET PROPELLANT INGREDIENTS AT
CRYOGENIC TEMPERATURES.

⑩ by Henry A. McGee, Jr.

Principal Investigator

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Henry A. McGee, Jr.
Principle Investigator

Final Scientific Report

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I. INTRODUCTION AND BACKGROUND INFORMATION

This research program has had two major thrusts: (1) the synthesis and characterization of unusual and high energy species by cryochemical techniques, and (2) the combustion of these species in laser cavities to explore their efficacy in producing population inversions for high powered chemical lasing. We utilized cryogenic techniques because our synthesis objectives were at the limit of the energy content even theoretically possible in a chemical system, and thus very low temperature environments were required to prevent the premature exothermic decomposition of the fuel or oxidizer.

This first Chapter will briefly review the synthetic chemical aspects of our work which has formed the necessary platform for the launching of chemical laser research.

Cryochemical Synthesis (General) - The motivation for high energy chemical research originally stemmed from a primary interest in propulsion. Weapons delivery depends upon chemical propulsion, and present limitations on range, speed, and payload can be overcome if new, more energetic propellant ingredients can be found. The most productive search will be by novel, more imaginative ideas and techniques for synthetic and chemical kinetic studies.

A mutually complementary experimental and theoretical program was conducted here. This study involved uniquely combined plasma or pyrolysis activation and cryoquench techniques to yield a number of small molecules, generally of the first row elements, which exhibit unusual reactivity and/or high energy content. A new semi-empirical and highly accurate molecular orbital computer program (also developed under AFOSR sponsorship at another institution) was used to aid in the selection of the candidate

molecules most likely to be successfully synthesized. The underlying objectives were then the synthesis of high energy molecules that would likely be stable only at cryogenic temperatures, and the subsequent characterization of these products from a molecular energetic and kinetic perspective.

This research program was one of basic chemistry, but it was conducted in the Chemical Engineering Department by research engineers. In a sense, therein lies a clue to the distinction between this AFOSR program and a perhaps similar appearing program sponsored by e.g., NSF, in an academic chemistry department. And that is, the efforts herein were motivated by a primary interest in the ultimate application or use of this science and not merely as a study of the science itself. This motivation permeated the research and strongly influenced the day-to-day decisions in the laboratory. For example, synthetic chemistry was a large part of this effort, but we employed only those synthetic methods that seemed to be generalizable, at least in principle, to large scale production. Without this capability, of course, the product species, no matter how interesting, would remain a laboratory curiosity.

Novel techniques of chemical synthesis, frequently using combined plasma and cryogenic techniques along with unique instrumentation were developed. Though no research is ever as fruitful as the investigators hope, these synthetic studies did yield some interesting product species and new insights. Our synthesis objectives were visionary and centered upon chemical energy storage in systems at the upper limit of such storage that is even theoretically possible. Unfortunately endothermicity and instability are almost synonyms, but with favorable kinetics, cryogenic synthesis and ordinary temperature existence are not necessarily

mutually exclusive characteristics. After all, even benzene is thermodynamically unstable relative to the elements at room temperature since its ΔG_f° is +31 Kcal/mole.

The broader understanding of chemical phenomena at very low temperatures is not restricted to these ideas in chemical energy storage, but rather such understanding is relevant to any engineering situation involving low temperature processes or operations. This occurs, for example, in the manufacture, storage and handling of common cryogenic fluids and propellants (such as liquid oxygen, liquid fluorine, and liquid hydrogen); in the problem of explosions in liquid air plants; and for all space activities both in orbit as well as on the moon where normal environmental temperatures can be very low. The techniques also represent a new dimension of preparative industrial chemistry even though it is still an embryonic one. Finally, a rather interesting and unexpected spin-off came in new inorganic polymeric materials for high temperature service, and these results are also summarized in this report.

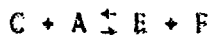
But a new and very provocative application of this new chemistry appeared a few years ago. Lasers! The first chemically pumped laser was reported in 1965 from vibrationally hot HCl formed by the pulsed reaction of photolytically produced Cl atoms with H_2 . For high energy density on a target over time, CW operation is essential, for all schemes that are inherently pulsed imply a low duty cycle and hence low average power. HF and CO were first made to lase in the CW mode in 1969, so CW chemical lasers are a new phenomenon. The very high energy molecules that had been synthesized by cryogenic procedures might conceivably produce intense population inversions when they were burned and thereby yield high powered wholly chemically pumped, CW lasers. Our somewhat unique orientation in the laser business was this expertise with unusual and

high energy chemistry. Our objectives in laser technology were the development of high power and high efficiency pumping reactions for possible application in weapons systems and in heating plasmas to fusion conditions. The weapons application suggests electronic inversions for reasons of less beam divergency, fewer problems of atmospheric windows, smaller optics, and, most significantly, higher energy density on the target. On the other hand, plasma heating requires a high powered, long wavelength laser. Our objectives were to study the efficacy of our unusual high energy chemistry in producing both electronic and vibrational inversions.

The partitioning of the exothermic energy of reaction into vibration, rotation, translation, or electronic excitation is determined by nature, or in a more theoretical vernacular, the partitioning results from the shape of the potential energy surface on which the reaction occurs. In quantum mechanical reactive scattering cross-section calculations performed in this laboratory (1), we have shown that so-called attractive potential energy surfaces are essential for the appearance of a large portion of the exothermicity as vibrational energy. Such potential energy surfaces show that the energy of reaction is released as the new bond is being formed rather than as the product species separate after the reactive collision has occurred. Our analyses also showed that reactions most favorable for vibrational excitation are those of very low activation energy which are also, of course, the fastest reactions as well. The chemistry of the labile and energetic cryo-reagents and other unusual compounds of interest in this research appear then to be ideally suited for pumping reactions of optimum efficiency.

Again, for background purposes, the following brief tutorial on cryochemistry has seemed to be appropriately included (2).

Even the simplest stoichiometric chemical reaction is the composite result of a complex array of concurrent, consecutive, and competing elementary reactions in each of which a single unimolecular or bimolecular event occurs. For purposes of discussion, a simple mechanism consisting of two reversible elementary reactions may be illustrated as follows:



The elucidation of such a reaction mechanism, i.e., the identification of each elementary molecular process and the study of the rate of each is, of course, the primary occupation of chemical kineticists. Remembering that the rate of each elementary reaction varies as

$$\text{Rate} \propto e^{-E_{\text{act}}/kT} \quad (2)$$

we note that the rate of any reaction with a finite activation energy may be reduced to zero by sufficient reduction of the temperature. Suppose product C is desired, but at room temperature the reaction produces E and F as the main products. The relative activation energies may be such that a lower temperature may exist which will still allow A and B to react to form C, but which will kinetically prohibit C from reacting further. If no temperature satisfies these requirements (as is often the case), then A and B may be encouraged to react whereupon C may be captured by quickly lowering the reaction temperature, i.e., by performing a cryoquench. By such schemes low temperature techniques permit the

preparation of highly reactive intermediates as stable reagents, for at cryogenic temperatures those particular reactions which would destroy the reactive or unstable compound may be frozen out.

A second consideration from Equations (1) and (2) concerns the complex mechanism in which a reduced temperature will slow each elementary reaction differently, depending upon its particular activation energy, and, in so doing, the reduced temperature will grossly alter the overall macroscopic product distribution. For example, HO_2 , a minor constituent present as an intermediate in the reaction of hydrogen and ozone to form water, will evidently dimerize at 77 K to produce not water at all, but rather hydrogen superperoxide, H_2O_4 , in good yield (3). The use of low temperatures in this manner to redirect chemical change is not limited to the production of exotic substances, for by identical arguments cryochemical technology also promises the synthesis of known substances from more direct and less expensive processes.

A third observation from Equation (2) is that "high" and "low" temperatures in chemistry have meaning only in the sense of a comparison of kT with E_{act} . Hence cryochemistry is but one part of the domain of chemistry under extreme conditions. Very similar in concept is the use of very high temperatures and even plasmas as a means of synthesis. In contrast to our previous examples, suppose in Equation (1) that room temperature favors equilibrium product C, while very high temperatures favor the desired product E. The desired high temperature equilibrium distribution may be frozen in by a cryoquench wherein shifts in equilibrium back to favor C that would accompany a more gentle cooling have again been kinetically blocked. When methane is heated above 3000°C , acetylene is

produced in thermodynamic equilibrium, and this endothermic species may be stabilized by utilizing cold gas injection, or liquid droplet injection, or by the use of a fluidized bed, or by any other fast quench technique. Both high and low temperature chemistry then are concerned with the syntheses beginning at high temperatures ($T > E_{\text{act}}/k$) but usually ending at a low temperature ($T < E_{\text{act}}/k$) to produce and stabilize molecules that would be otherwise troublesome or perhaps even unobtainable.

Few ordinary room temperature reagents will react at cryogenic temperatures without some sort of an activation. Hydrogen and fluorine when precooled to cryogenic temperatures will ignite on contact, but this sort of reactivity is rare. A generalized cryochemical reaction system for the more usual situation in which activation is required is shown schematically in Figure 1.

The objective is to produce a free radical or an electronically excited, or perhaps only vibrationally excited, species by some activation process and to then contact that species with a second reagent either in a cryogenic environment or in a subsequent cryoquench arrangement. With both reagents precooled the reaction mechanism will be arrested at the point of that elementary process in which $E_{\text{act}} > kT$ at the particular temperature of the cryo-reactor. The activation operation can take many forms - electric arc discharge, electrodeless radiofrequency discharge, pyrolysis, photolysis, and others. This activated gas, which is itself continuously reacting back to some lower energy configuration, must be rapidly conducted into the cryogenically cooled reactor. For example, although molecular hydrogen is rather unreactive, atomic hydrogen reacts vigorously with many substances at cryogenic temperatures. But since

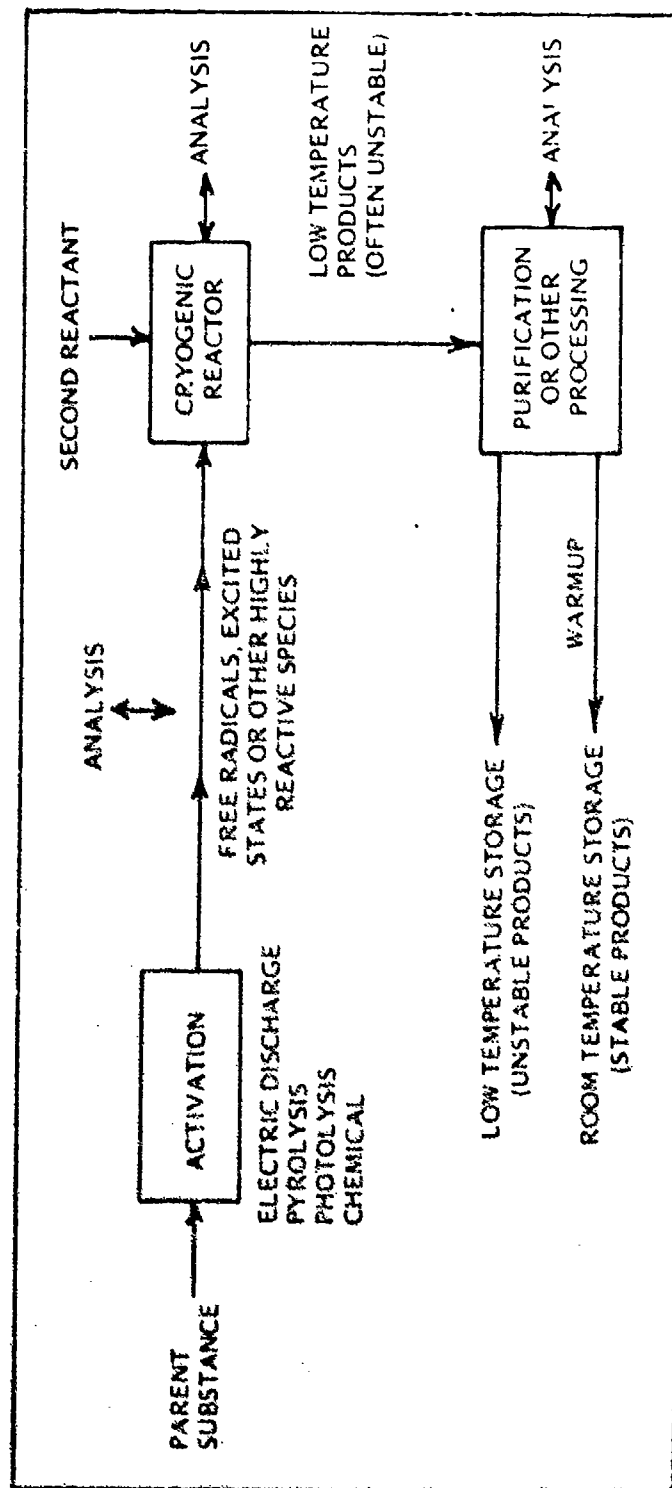
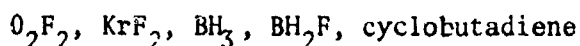


Figure 1. Generalized cryochemical reaction system.

atomic hydrogen rapidly recombines, it is essential to transport it from its point of generation to its point of cryoreaction as fast as possible. If the product species are unstable at ordinary temperatures, all subsequent processing of the cold product mass must, of course, also be conducted at controlled low temperatures. These techniques have been used in this laboratory to successfully synthesize and study previously unknown compounds typified by,



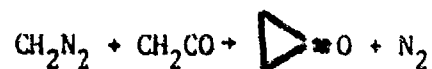
and many others (4).

Another variation of the cryogenic technique involving thermal activation is to quench and thereby stabilize as condensed phases species which are known only in high temperature vapors or plasmas, such as S_2 , SiF_2 , BF , etc. For example, from such experiments a new form of sulfur has been reported which is observed to melt at 213 K (5). Evidently S_2 , analogous to O_2 , has been prepared.

Very reactive species which are frequently postulated by chemists as reaction intermediates but never before isolated, have been directly observed and stabilized by cryochemical techniques (6). Three compounds of this class are: cyclobutadiene, N_2H_2 , and cyclopropanone. The intermediate diimide N_2H_2 , which reacts with itself at 158 K to form hydrazine, N_2H_4 and nitrogen, can be synthesized by the reaction of atomic oxygen from an electrodeless discharge with NH_3 followed by a rapid cryoquench. The rapid quench evidently slows the further oxidation of the intermediate NH radical which permits its dimerization and the subsequent stabilization of the reactive product, N_2H_2 . That is, kT

has been made small relative to the activation energy of the hydrazine reaction which would destroy the product. Similarly, when oxygen atoms are reacted with ethylene and followed by a cryoquench, large amounts of ethylene oxide are produced whereas only trace amounts are produced at more ordinary temperatures. This notion of arresting a reaction part-way through is a perfectly general characteristic of cryochemical processes.

Some few reactions are known to occur at low temperatures without external activation. For example, a liquid-liquid, solvent free reaction of diazomethane with ketene at 128 K produces a stable, unreactive solid, cyclopropanone,



which has been long postulated as an intermediate in reaction mechanisms by organic chemists. It has only recently been produced, isolated and studied by these new cryochemical techniques (7). Although it remains stable indefinitely as a solid below 183 K and it can be transferred through glassware in vacuum rack manipulations, a white polymer is always left behind where the ketone had been condensed.

Thus, these techniques which produce as useful reagents both totally new species and reactive intermediates, and which as well open new routes to well known compounds - all invite adaptation to large scale industrial production. The largest single factor presently deterring this adaptation appears to lie, not in the cryogenic engineering at all, but rather in the production of the active species. The economic production of

active species for a variety of applications, not just those in cryochemistry, is an active area of research.

Many unconventional design and analysis problems can be anticipated in large scale cryochemical operations. Design problems in heat exchange are apparent if a high energy activation is to be physically close to a cryogenic reactor. Also energy exchange with large temperature differences and correspondingly large entropy increases will cause large thermodynamic inefficiencies in these as well as in any quench operation. Compositional analysis of such cryogenic mixtures is clearly imperative for process control, but such analysis must be conducted without warmup, for the act of warming will often destroy the sought-for product. Separation processes will require new developments in apparatus and procedures to handle unstable, highly reactive substances which must, at no point, be warmed above some very low temperature. Little design and development work on separation apparatus and techniques has been done on even laboratory scale operations. The new products may also require storage at very low temperatures, but this, although certainly a nuisance factor, seems of no great consequence from a technical point of view.

We have adapted the mass spectrometer to cryochemical technology as a powerful tool of physical analysis by arranging to inject a cold sample directly into the ionizing electron beam of the ion source. The mass spectrometer offers simple and direct analysis which leaves little doubt as to the identification of the compounds that are present whether or not they have ever been previously observed. In the research laboratory,

the mass spectrometer also enables one to study the molecular energetics and structure of these unusual compounds (8).

The high energy content of many cryochemical compounds suggests their application in propulsion. Within the interesting family of oxygen fluorides, O_3F_2 , which may not even be a single compound, is a blood-red liquid at 90 K that decomposes rapidly above 115 K (9). A saturated solution of 0.1 percent O_3F_2 in LOX is hypergolic with hydrocarbons, and a semi-continuous processing unit operating at cryogenic temperatures for the production of pilot quantities of O_3F_2 - LOX solutions has been developed (10). Design problems included features needed to (1) combat the critical temperature-dependent decomposition characteristics and safety hazards, (2) the low temperature reactor design which involved an electric discharge in the mixed elements at cryogenic temperature, and (3) problems in chemical analysis. The plant successfully produced 4 GPH of an almost saturated solution. The family of nitrogen-oxygen-fluorine compounds is of interest because of the possibility of combining the oxidizing properties of several different O-F groups with the stability of nitrogen. The idea is to use the nitrogen atoms in the candidate molecules as a sort of substrate onto which are hung the sought-for O-F groups.

Complementing these oxidizers, several less stable boron hydrides (BH_3 , BH) have received attention as possible high energy fuels. These species may be made from diborane (B_2H_6), from direct reaction of hydrogen with boron, or by other means. Any species having a high concentration of hydrogen per cm^3 will, of course, be interesting as a fuel, particularly if it also involves an endothermic molecule. But

endothermic molecules exhibiting an enhanced chemical valence are precisely the class of substances with which cryochemical techniques are most appropriate.

Cursory Summary of Synthesis Work on this Program

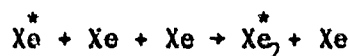
Several contributions to cryochemical understanding from this laboratory and which were developed under AFOSR sponsorship are collected in Appendix A of this final scientific report. As may be inferred from these sample papers, much of the success in chemical synthesis that we have achieved can be traced to the design and development of a versatile cryogenic reactor-mass spectrometric inlet arrangement which we feel to be a significant contribution both to mass spectrometric technique and to the technology of cryochemical research and development (11). Earlier designs were essentially glorified traps with built-in, but very carefully designed, mass spectrometric probes (12). But our latest designs employ any sort of reactor, followed by any simple processing, and continuous mass spectrometric monitoring at any point with no attendant warm-up from the cryogenic operating temperature level. All three functions of reaction, processing, and analysis are effectively immersed in a liquid refrigerant (usually a 2:1 mixture of isopentane and 2-methyl pentane respectively which is useful to -168° , or a mixture of Freons, or other liquids) which can be automatically thermostated at any desired temperature level. In this facility we have successfully employed gaseous discharge reactors, pyrolysis reactors, and submerged arc reactors - each operating in a cryogenic environment. These cryo-reactors, in varying degree, physically superimpose the operations of high energy excitation and cryogenic quench (see Figure 1).

Noble Gas Compounds: - Experimental efforts to form noble gas compounds have a very long history, and the advantages of such species as propellants were first discussed by McGee almost twenty years ago (13). The molecular energetics are such that an excited helium atom, either alone or stabilized by combination with an H or F atom, would represent the most energetic chemical propellant even theoretically possible. Although theoretically exciting, the data and conclusions from all of the experimental research on the preparation of such species have been poor or equivocal. But the scientific community was shocked when Barlett in 1962 produced a white solid, stable at room temperature, from red gaseous PtF_6 and colorless Xe. It was XePtF_6 -- the first confirmed noble gas compound.

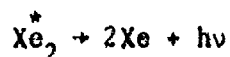
As part of this AFOSR program, a number of novel synthesis experiments aimed principally at postulated neon, argon, and krypton oxides and fluorides were conducted. These experiments involved such things as exploding wires immersed in liquid argon-fluorine solutions, similar submerged DC arcs, and cryoquenched low pressure gaseous discharges. There was never even a hint of successful synthesis except in the production of KrF_2 (14). This compound had been reported previously, but it was possible to develop its molecular energetics from ionization efficiency measurements (14). This noble gas compound phase of our synthesis research was reluctantly discontinued.

It is interesting however to note that exciplexes formed from noble gas atoms are being studied as sources for high powered lasing for application in controlled thermonuclear fusion (15). The idea here is to make use of this same high energy storage that noble gas compounds represent, and, since these species have no stable ground

state, the stimulated emission will not destroy the population inversion. Thus the exciplex laser attempts to take advantage of the very characteristic, chemical instability, that the cryochemical preparative schemes sought to freeze in. The extraordinary energy storage potential is evident when one realizes that at a pressure of one atmosphere, excited dimers contain nearly 50 Kj/liter. Consider for example,



which can radiate via,



where we may imagine Xe_2^* acting as a nucleus for a single orbiting electron. Since there is no stable ground state, build up of population in the lower level cannot occur, and all of the inversion (rather than 50 percent) is available, in principle, to produce lasing. Other examples are Kr_2^* , LiXe^* , and HgXe^* . The properties of such species has been recently reviewed (15).

Boron Hydrides: - Both BH and BH_3 are extraordinarily reactive fuels, they are ground state singlets, that is, they are not free radicals, and hence we expect that it may be possible to isolate these species at very low temperatures.

Earlier work on the isolation and characterization of BH_3 as a cryochemical reagent (16) was expanded with considerable success (17).

Pyrolysis of BH_3CO proved to be a convenient source of BH_3 . Analysis of ionization efficiency measurements permitted the development of the

molecular energetics of BH_3CO , and, together with other data, a verification of our earlier energetic results on the BH_3 ; B_2H_6 system. The symmetric dissociation energy of B_2H_6 was established as 59 kcal/mole, and thus the specific enthalpy of, e.g., the $\text{BH}_3\text{-O}_2$ flame gas will be greater than from the similar combustion of B_2H_6 by 59 kcal/mole.

Unfortunately, our cryogenic rate data also suggest that borane, BH_3 , is lost by dimerization at temperatures where its vapor pressure is only about 10^{-5} torr, and hence its practical utility seems nil. Research on this very interesting species was then discontinued. In a similar vein, B_4H_8 , normally considered to be a reaction intermediate, was also stabilized at very low temperatures (18).

B-N Chemistry: - Our interest in the chemistry of boron prompted a series of exploratory experiments to produce and characterize the simplest B-N based hydrocarbon analogs. These explorations were successful, and, as we will now see, opened a whole new area of this initially solely energetic program to also include research with a new family of inorganic polymers.

It has long been recognized and elaborately discussed that BN should exhibit a similar chemistry to that of its isoelectronic counterpart C_2 , that is, BN chemistry and organic chemistry should be analogous. A large number of BN compounds corresponding to their isosteric organic analogs have been synthesized, but the basic building blocks of such a chemistry, iminoborane, HBNH , and aminoborane, H_2BNH_2 , have eluded synthesis because of their extreme reactivity. One expects these two compounds to be acetylene-like and ethylene-like respectively. Using our combined cold-plasma and cryogenic quench techniques, we have been

able to synthesize, isolate, and characterize H_2BNH_2 , but $HBNH$ has continued to elude our synthetic procedures (19).

It has also been possible to synthesize and partially characterize the substituted compound Cl_2BNH_2 and possibly $HClBNH_2$ (20). These compounds are simply made from the gas phase reaction of BCl_3 and NH_3 .

H_2BNH_2 and $HClBNH_2$ are isoelectronic with ethylene and vinyl chloride respectively, and we have polymerized both of these species to form materials presumably similar to polyethylene and polyvinylchloride. A characterization of these new polymers has been published, and it is possible that these discoveries will permit advances in new materials development, particularly in materials for high temperature service (21).

N-O-F Compounds: - Energetic arguments from many perspectives confirm that certain N-O-F compounds offer the greatest potentialities as high energy oxidizers.

All five of the heretofore known N-O-F compounds have been synthesized in good yield and characterized by their heretofore essentially unknown mass spectra (22). The molecular energetics of each compound has been developed from ionization efficiency measurements on the principle ions produced by electron impact dissociative ionization (22). With only one exception these mass spectra were previously unknown as was the bulk of the energetic information. In addition, a new compound, O_2NNF_2 , was synthesized in good yield, and it was mass spectrometrically and energetically characterized. O_2NNF_2 is a white solid at $-196^\circ C$ that decomposes into N_2F_4 and NO_2 even at $-130^\circ C$. Studies of both this new compound and the related $ONNF_2$ would have been impossible without a cryogenic reaction

facility since both are too reactive to exist except at very low temperatures. Several theoretical models including both the double-quartet idea and the MINDO molecular orbital scheme have been applied to the N-O-F family of known and postulated compounds with encouraging results. Thus it has been possible to predict the heats of formation and ionization potentials of numerous conceivable, but presently unknown, N-O-F compounds. These data then permit arguments as to the probable synthetic success with these hypothetical high energy N-C-F compounds.

Cryogenic Submerged Combustion: - Some effort has continued toward the discovery of new cryogenically cooled reactor configurations. In considering a physical superposition of activation and quench (see Figure 1), we have studied the submerged arc and the submerged flame. In both ideas, active species are continuously generated which then immediately react in the cold environment to produce the species of interest. The quench rates should also be high since the compounds to be quenched or deactivated are in direct contact with the heat sink - the boiling cryogen.

The schematic of the apparatus appears in Figure 2. The principle components consist of fuel and oxidant lines, a hand torch, and a nozzle that is attached to the bottom of the reactor. The oxidant and the fuel, are premixed at the torch handle before they reach the nozzle, and the mixed gases are ignited by means of an electrically heated nichrome wire over the port of the nozzle. After the nichrome ignitor is withdrawn from the reactor, the flame is adjusted to any desired stoichiometric ratio using control needle valves and rotameters, and liquid nitrogen is poured slowly into the reactor to ensure that the liquid initially

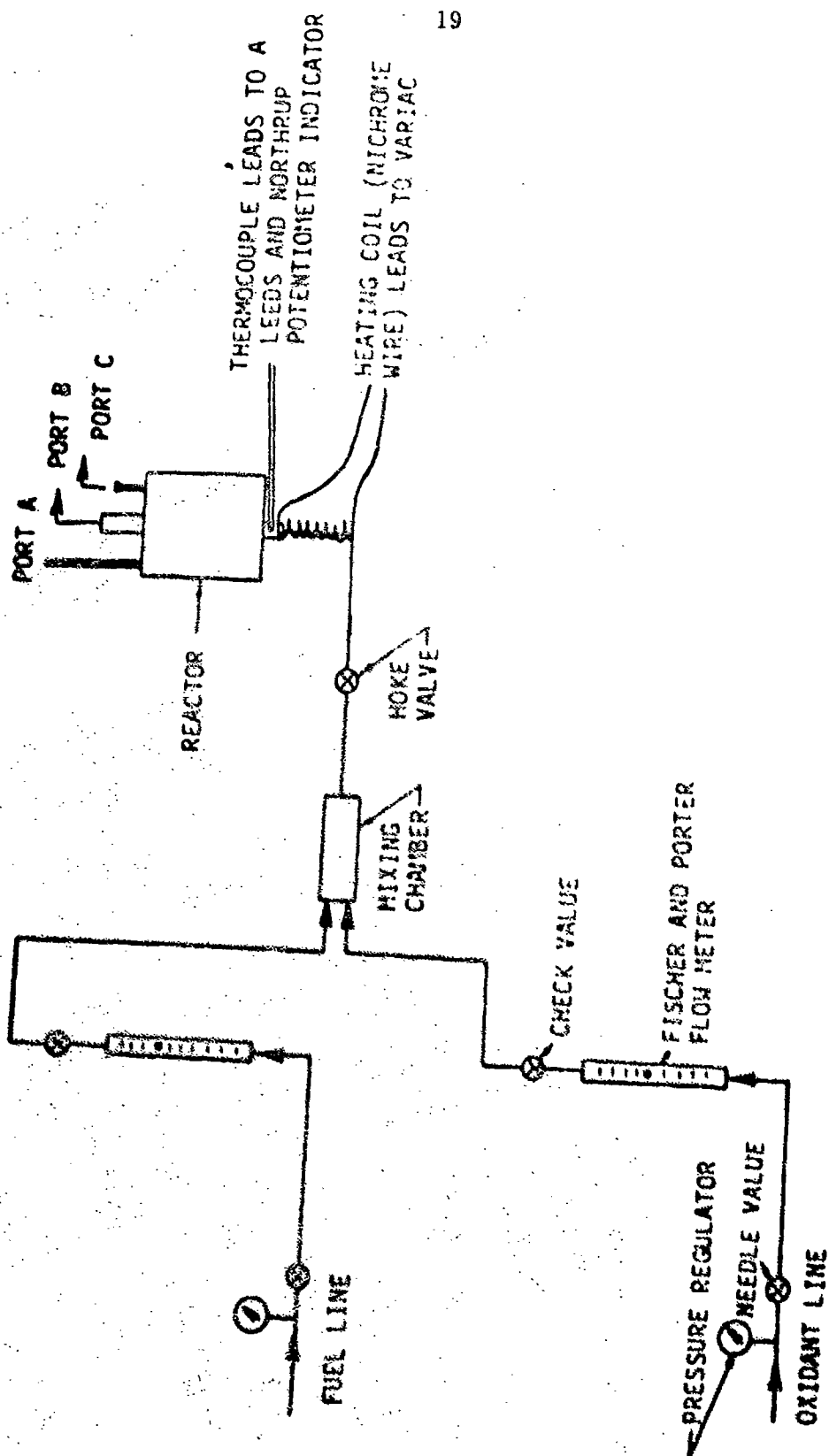


Figure 2. Reactant Flow Arrangement of Cryogenic Submerged Flame System.

in contact with the room temperature surfaces of the reactor, does not extinguish the flame by its rapid boiling. Also an 1/8 in high dam surrounds the nozzle port to prevent "pinching" of the flame by the nitrogen bubbles. The brass reactor has a plexiglass window to permit observation of the flame. Three openings at the top of the closed reactor vessel provide for the introduction of liquid nitrogen, for nitrogen gas and combustion gas venting, and for the introduction of the reaction products into the mass spectrometer for analysis. The reactor walls are insulated with styrofoam. Since a cold flame holder cannot support a flame, the temperature of the flame port is controlled by a nichrome wire heater controlled by a variac and a copper-constantan thermocouple connected to a potentiometer.

Only a few previous such studies have been reported long ago, and all involved diffusion flames: an H_2 flame in liquid air produced NO and O_3 (23), an H_2 flame in LOX produced O_3 (23, 24), an acetylene flame in liquid air produced HNO_3 and O_3 (25), and an H_2S flame in liquid air produced O_3 (25). Of course, in all experiments the major products were CO_2 and H_2O . As initial experiments, we looked at premixed flames of CH_4 , C_3H_8 , and C_2H_2 with O_2 that were operated submerged in liquid nitrogen. Each flame produced NO, N_2O , and NO_2 as revealed by mass spectral analysis of the products as they sequentially vaporized as the reactor was warmed from its operating temperature of 77 K to room temperature. The nitrogen oxides are not produced in combustion experiments with the same species under ordinary flame conditions. The technique then well demonstrates the alteration of kinetic pathways by extreme cooling.

Theoretical Research: - The theoretical component of this AFOSR research program has employed semi-empirical LCAO-MO-SCF computational techniques to calculate both heats of formation and ionization potentials. The so-called MINDO (Modified Intermediate Neglect of Differential Overlap) technique has been under continuous development by Professor M.J.S. Dewar and his associates at the University of Texas for several years (26). Although it has not yet been so recognized, this work (also under AFOSR sponsorship) is of great practical significance since for the first time it allows one to make quantum chemical calculations of thermodynamic quantities to within chemically significant accuracies. The theory was developed for organic compounds, but we have successfully applied the ideas and approximations to B-H-F compounds as well (27).

Some idea of the accuracy that one may expect from the MINDO scheme is apparent from Table I which summarizes some of our results on N-O-F compounds. No data on the last seven compounds appearing in Table I were used in calculating the listed values of ΔH_f° . These are then bona fide predictions, and with only one exception, agreement with experiment is good. The other eleven compounds in Table I are totally unknown. Arguing from just the exothermicity of postulated decomposition processes, that is, using the Thomsen-Berthelot rule, we may conclude that of this list, FONO, FO₂NO, F₂N(OF), and F₂N(O₂F) should be marginally stable. Shortly after this prediction, Schumacher reported the synthesis of FONO (28). This is comforting and adds one more indication of the power of the semi-empirical formalism. In this particular case however, none of the predicted species seem particularly exciting; because of their relatively low endothermicity.

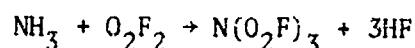
Table I

Heats of Formation of Postulated and Known N-O-F Compounds^a

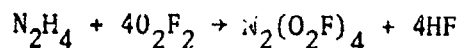
compound	ΔH_f (kcal/mole)	ΔH_f (kcal/mole)
	MINDO	exp.
FO NO	7.59	
FO ₂ NO	-31.10	
F ₂ NONF ₂	21.69	
F ₂ NO ₂ NF ₂	37.12	
ONNFNFNO	78.80	
F ₂ N(OF)	-20.48	
FN(OF) ₂	- 9.87	
N(OF) ₃	6.56	
F ₂ N(O ₂ F)	7.88	
FN(O ₂ F) ₂	74.02	
N(O ₂ F) ₃	140.1	
<hr/>		
FNO ₂	-31.48	-25 to -33.8
FO NO ₂	1.50	2.5
ONF ₃	-33.31	-34.1
ONNF ₂	18.21	18.9
O ₂ NNF ₂	-14.67	0
FN NF	19.45	19.4
F ₂ NF ₂	- 2.81	- 5.0

^a Abstracted from P. S. Ganguli and H. A. McGee, Jr., Inorg. Chem. **11**, 3071 (1972).

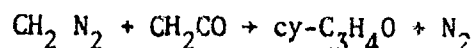
We could well imagine controlled cryogenic synthesis procedures like,



or



but the theoretical arguments would suggest that one substitution of the O_2F moiety in NH_3 or two in N_2H_4 is more reasonable. Such reactions appear startling to be sure, but they are not at all unlike our earlier successful coreaction,



The point is merely that the experimental and the newly available and accurate theory support and guide each other.

Dewar and his colleagues have, of course, applied their method to a much broader series of compounds, and we present in Figure 3 a summary of their calculations of heats of formation on 193 compounds that allows a quick visual assessment of the very great accuracy that the Texas group has achieved.

The MINDO program determines the energy of a species, and thus its heat of formation, by optimizing its geometry such as to obtain that structure of minimum energy. With the molecular structure thus in hand, it is also possible to use the MINDO scheme to calculate force constants, and, from that, the normal vibration frequencies of a molecule (29). And, of course, if you know the heat of formation, the structure, and

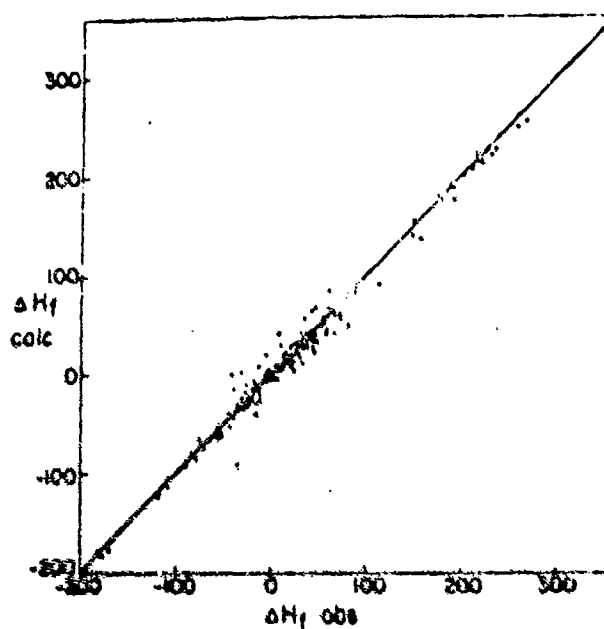


Figure 3. Plot of calculated vs. observed heats of formation (ΔH_f , kcal/mol at 25°C) for 193 compounds derived from H, C, N, O, F, Si, P, S, and Cl, using MINDO. Taken from M.J.S. Dewar, Science 187, 1037 (1975).

the vibration frequencies, one may immediately calculate the thermodynamic properties of the species as an ideal gas at all temperatures and pressures using the formalism of statistical thermodynamics. For example, the partition function, f , for any non-linear molecule containing n atoms is,

$$f = g_0 \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \frac{V_A}{n} \frac{\pi^{1/2} (\sigma \pi^2 k T)^{1/2} (I_A I_B I_C)^{1/2}}{h^3 \sigma} \prod_{3n-6} \left(1 - e^{-h\nu_i/kT} \right)^{-1} \quad (3)$$

where g_0 is the multiplicity of the ground electronic state, n is Avogadro's number if we are concerned with the properties of a mole of the species, σ is the symmetry number (determined by inspection from the overall molecular structure), $I_A I_B I_C$ is the product of the three principal moments of inertia, the ν_i are the $3n-6$ characteristic vibration frequencies, and all of the other symbols have their usual meaning. We may express all of the thermodynamic properties as functions of $\ln f$ and its derivatives. For example

$$(H^\circ - H_0^\circ)/T = R \left[T \left(\frac{\partial \ln f}{\partial T} \right) + 1 \right] \quad (4)$$

or in terms of practical units, we can write,

$$\begin{aligned}
 S^\circ(\text{trans}) &= \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln p(\text{atm}) - 2.315 \\
 S^\circ(\text{rot}) &= \frac{3}{2} R \ln M + 4 R \ln T + \frac{1}{2} R \ln I_A I_B I_C \\
 &\quad - R \ln \sigma + 265.330 \quad (5) \\
 S^\circ(\text{vib}) &= R \sum_{i=1}^{3n-6} \left[\left(\frac{h\nu_i}{kT} \right) \left(e^{\frac{h\nu_i}{kT}} - 1 \right)^{-1} - \ln \left(1 - e^{-\frac{h\nu_i}{kT}} \right) \right]
 \end{aligned}$$

and similarly for all of the thermodynamic properties. The important point to realize is that all of the thermodynamics of ideal gases is immediately calculable from the molecular architecture and the vibration frequencies. And this is exactly what MINDO gives to us. As an example of typical accuracies that may be expected, Table II presents comparisons of experimental and theoretical absolute entropies and heat capacities for several compounds. Recall that the only input information in these calculations is just the gross structure of the species.

The MINDO formalism is not at all limited to the calculation of thermodynamic quantities. In connection with our cryogenic stabilization experiments, we had predicted the activation energy for the dimerization of borane, $2\text{BH}_3 + \text{B}_2\text{H}_6$, to be 1.86 Kcal shortly before it was measured in another laboratory to be 0 ± 2 Kcal from a gas phase kinetic study at ordinary temperatures (30). Again, the Texas group has calculated activation energies for many reactions, and for emphasis some few of these are summarized in Table III.

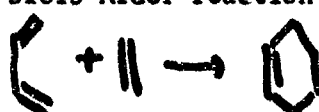



Table II
Calculated and Observed Entropies and Heat
Capacities at 298 K^a

Compound	S ^o (cal/mole K)		C _p ^o (cal/mole K)	
	obs	MINDO	obs	MINDO
H ₂ O	45.1	45.0	8.0	8.0
NH ₃	46.0	46.0	8.5	8.4
CS ₂	56.8	57.4	10.9	11.3
CH ₂ N ₂	58.0	58.7	12.5	13.0
C ₂ H ₂	48.0	48.3	10.5	10.6
CH ₂ CO	57.8	58.3	12.4	12.9
CH ₂ CH ₂	52.4	52.6	10.2	11.0
cy-C ₃ H ₆	56.6	56.9	13.1	13.7

^aAbstracted from a preprint by M.J.S. Dewar and G.P. Ford that was kindly supplied by the authors in advance of publication.

Table III

Comparison of Calculated and Observed Activation Energies of Reactions^a

Reaction	Activation energy (kcal/mole)	
	Observed	MINDO
Rotation about C=C bond in $\text{H}_2\text{C}=\text{CH}_2$	65.0	63.9
$\text{H}_3\text{C} + \text{H} - \text{CH}_3 \rightarrow \text{H}_3\text{C} - \text{H} + \text{CH}_3$	11.5	14.8
Diels-Alder reaction		
	28.2	27.5
	62.5	62.0
	23.0	27.3
	24.6	28.3

^aAbstracted from M.J.S. Dewar, Science 187, 1037 (1975).

II. CRYOCHEMICAL LASING

As we have seen in Chapter I, combined plasma and cryochemical techniques represent the current best available means to synthesize and isolate the most energetic and reactive compounds that chemistry affords. For example, O_2F_2 can be imagined as two "stabilized" F atoms wherein we have had to pay only a small energy penalty (0.8 eV in this case) in using an O_2 molecule to act as a carrier for the F atoms. The use of such reagents suggests that we should be able to construct all-chemical lasers, with no prerequisite photolytic or electric discharge techniques. Some typical examples of these interesting and unusual molecules are listed in Table IV.

In a single sentence, our objective has been to study the combustion of these sorts of unusual compounds in our laser facilities in an attempt to discover new CW visible and infrared lasers of high energy efficiency.

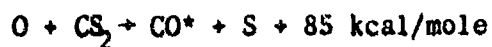
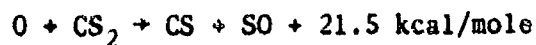
Certainly the use of these compounds will be a nuisance since they frequently must be synthesized by unusual and complex procedures, and sometimes they must even be kept cold (less than $-150^{\circ}C$) if they are to be stabilized. Inadvertent warming will not only result in the loss of the reagent, but frequently in explosions as well. Nuisance is then a well-chosen descriptor. The counterbalancing influence is the realization that these molecules represent the limit of the chemists' ability to both store energy and to produce fast reactions.

Table IV
Some Unusual Compounds from Cryochemical
and Related Synthesis Procedures

N_2H_2	NH_4O_3	CS
O_2F_2	HN_3	Na_2
O_3F_2	KrF_2	NCN_3
H_2O_4	ONF_3	C_3O_2
BH_3	O_2NNF_2	O_3
FN_3	HNO	SiF_2
	TiH_4	BF

CS SYSTEM

Since the ultimate aim of this research has been to explore the realm of cryogenic synthesis for new reactants for pumping chemical lasers, a major prerequisite was dependable, efficient apparatus. To test the apparatus a reliable laser pumping reaction has to be employed. Previous studies have shown that the CO laser pumped by the reaction of CS₂ with atomic oxygen is such a reliable system (31, 32). The reaction is believed to follow the sequence:



(6)

It has been shown that the first step acts as a rate limiting step for the pumping reaction and that its exothermicity reduces laser gain (33). Also, it is believed that 75 percent of the exothermicity of the second reaction appears as vibrational excitation of CO.

While a dependable laser cavity and support apparatus were being fabricated and tested, an attempt at eliminating the first reaction step was also tried. It was already known that CS could be made from CS₂ using a radio frequency discharge in flowing CS₂ vapor and that the undissociated CS₂ that survived the plasma could be removed from the newly formed CS by cryogenic trapping. However, it was not known whether sufficient quantities of CS could be made by these techniques for direct use in the laser.

Sir James Dewar, the first cryochemist, discovered about the turn of the century that solid CS could be prepared by this discharge technique,

that it could be frozen out at liquid air temperatures, and that upon slight warming still at cryogenic temperatures the substance would produce a violent explosion and a flash of light. This observation is all the more remarkable when one realizes that Dewar had just a year or so before liquefied oxygen and nitrogen for the first time in history.

Our initial objective then was the restudy of the CS_2/O system followed by an adaptation of the cryogenic synthesis scheme to then study the pure CS_2/O system.

Apparatus: - A 15 x 16 cm I-beam 1.8 m long is used as an optical bench, Figure 4. Mirror detectors and reaction tube are clamped to this bench using suitable mounts. The laser cavity consists of two mirrors 1.55 m apart with the reaction tube located in the center. One plane mirror and one 3 m spherical mirror - both gold coated - are used to immitate a true confocal spherical interferometer. With this arrangement the mirrors are not required to be perfect matches in order to minimize losses (34). Both mirrors are held in Oriel precision mirror mounts (Model B-44-60) which are mounted on Oriel (B-62-60) translation stages clamped to the optical bench. The plane mirror has a 1 mm hole through the center for coupling the laser output either to a power meter or to a monochromator.

The reaction tube, Figure 5, consists of a 2.54 cm ID pyrex tube with o-ring seals for attaching two atomic oxygen generators and two CaF_2 Brewster windows. There are also two side arms for CS_2 supply, one port for pressure monitoring, and an exhaust port to the pump. Teflon plugs - located at each of the CS_2 supply ports - are used to inject the CS_2

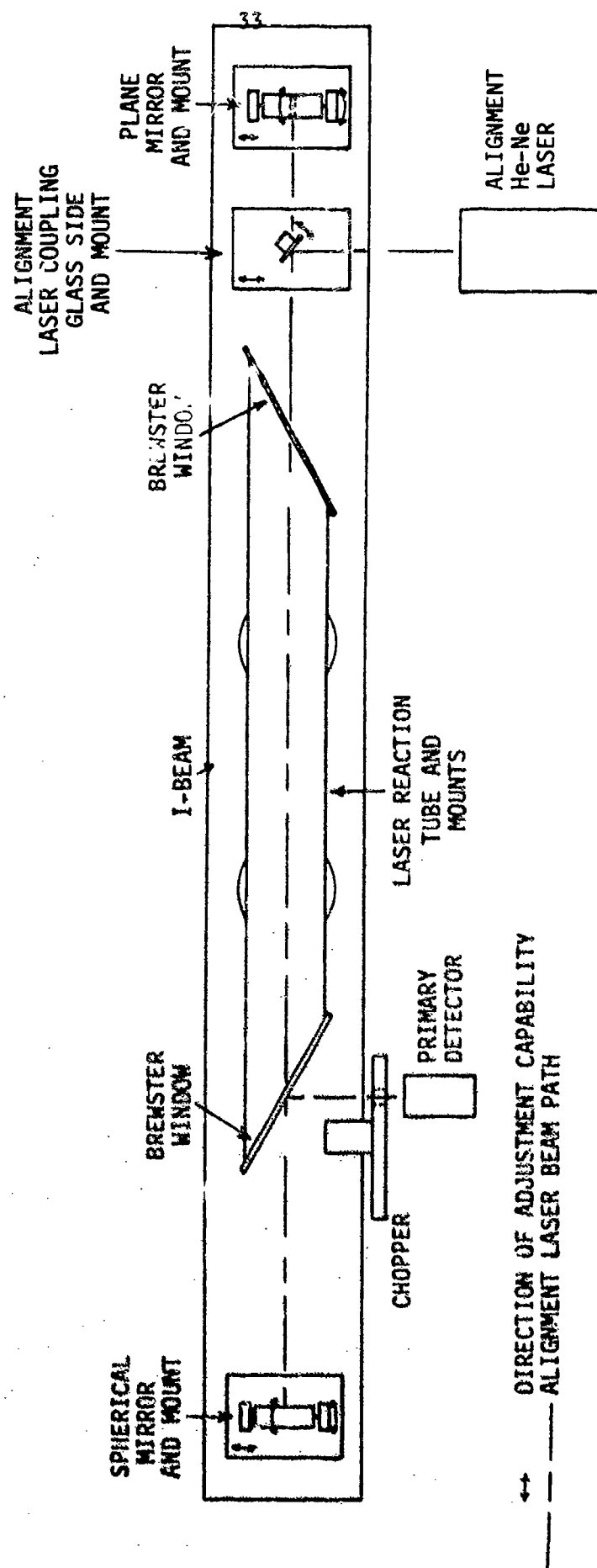


Figure 4. Optical arrangement of the laser cavity showing alignment and detection devices.

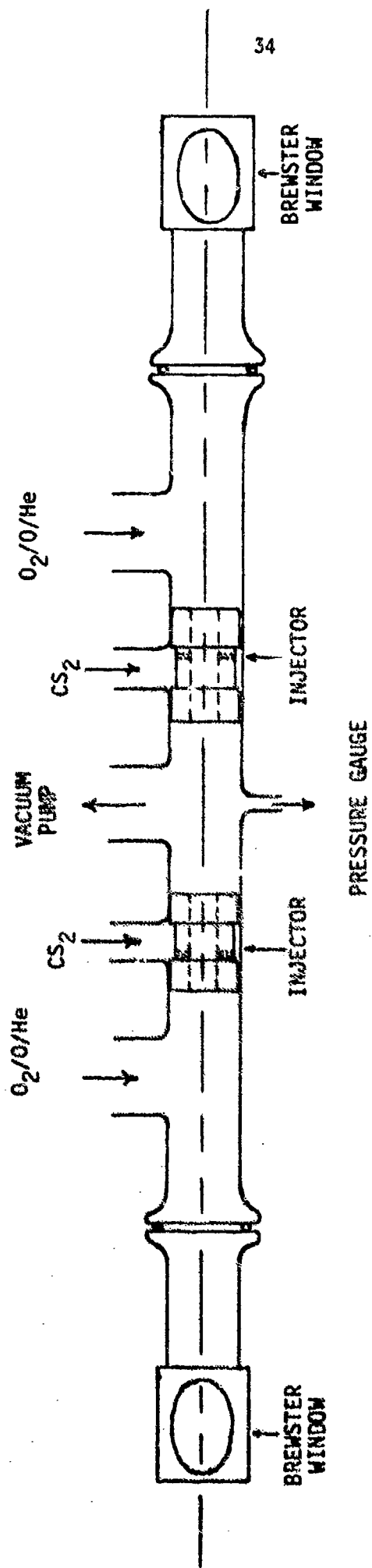


Figure 5. Detail of laser reaction tube (not drawn to scale).

into the flowing atomic oxygen stream in a manner which well mixes the two reactants. The first studies were made on a reaction vessel in which the $0;0_2;He$ mixture was pumped down the laser tube, and the CS_2 was merely injected through a side-arm. The flow pattern of reacting gases in this vessel was quite unsymmetrical, lying mainly along the half of the 1 cm ID reactor nearest the side-arm, as was conveniently indicated by the visible SO_2 afterglow. The lasing signal was not continuous, but rather it appeared pulsed indicating that a greater inversion of CO was present only during the high voltage peaks of the 60 Hz discharge that powered the atomic oxygen generator.

In order to provide a more uniform mixing of reactants, a Teflon injector 4.5 cm long with 5 equidistant radial holes for the fuel was fabricated so as to induce a swirling injection of the CS_2 into the flowing oxidant. This injector was placed at the CS_2 inlet, inside the reaction tube. The Teflon injector produced a more homogeneous flame, but its narrow internal diameter (6 mm) may have inhibited or choked reactant flow to such an extent that any positive effects from the more uniform mixing of reactants may have been cancelled out.

The entire arrangement is such that two flames are produced and aimed at each other. Located half way between the two flame injectors is the pump line. This configuration eliminated contamination of the Brewster windows by reaction products, one of which is elemental sulphur, which severely coats the interior of the flame reactor. This sulphur is however readily removed between runs by merely pumping atomic oxygen through the reactor.

Atomic oxygen is produced from molecular oxygen in two Woods tubes using high voltage 60 Hz discharges. The discharges are produced

by neon sign transformers (15 KV and 120 mA maximum) driven by variable auto-transformers (Powerstat, 20 Amp maximum load). In order to reduce recombination of the atomic oxygen, helium is mixed with the molecular oxygen before entering the Woods tubes.

Production of CS from CS₂ is accomplished in a fused quartz tube with 2.2 cm ID and 50 cm length. Three methods of dissociation are used. The first is a radio frequency discharge provided by a 2 KW RF generator (Heathkit DX608 transmitter and Collins 30S-1 RF power amplifier). The RF energy is coupled to the gas flowing in the tube capacitively using two 1 cm wide bands around the tube. Many attempts to inductively couple the power were unsuccessful due to the fact that the energy in this configuration was confined to a thin region through the center of the tube. The second method of dissociating the CS₂ is by use of a high voltage 60 Hz discharge like those used with the Woods tubes mentioned above. Energy is coupled to the gas by means of metal fittings in contact with the gas at either end of the fused quartz tube. One fitting is stationary and the other is constructed such that a ring shaped electrode could slide into the tube to allow for an adjustable discharge length and thereby a variable contact time of the flowing CS₂ in the plasma. In the third method of dissociation, CS₂ was passed over tungsten filaments electrically heated to 1300°C as revealed with an optical pyrometer.

Pumping of the apparatus is provided by a 250 cfm rotary vacuum pump (Beach-Russ RP 250). The pump is protected from solids and harmful condensables by a liquid nitrogen cold-finger type trap and a wire screen. This trapping is necessary, for in earlier experiments with no protection for the pump, sulphur gradually deposited in the

pump eventually causing one of the vanes to freeze and necessitating a complete overhaul of the pump.

Laser output is monitored primarily by a pyroelectric detector (Laser Precision Model KT-4010) arranged to receive reflected lasing from one of the Brewster windows. Another pyroelectric detector (Laser Precision Model KT 4010 cx) and a power meter (Jodan Model PM 550) are used at various times to monitor output through the 1 mm hole in the flat mirror. A variable speed chopper (Laser Precision Model CTX534) is used to chop the CW laser output for the pyroelectric detectors. The detectors were arranged for either oscilloscope display or direct recording. In some experiments, the laser output was also passed through a monochromator (Perkin-Elmer Model E-1 modified for automatic scanning) the signal from which was monitored by one of the pyroelectric detectors. The detector has a current responsivity of about $1 \mu\text{A/watt}$ when the signal is chopped at 10-50 Hz, and a preamplifier converts this to a voltage responsivity at a conveniently low output impedance of 3K ohms. The preamp was found to be unnecessarily noisy. Simply replacing this by a battery system, permitted reliable readings at 100 nanowatts incident power. This is revealed by noting the reading on the oscilloscope or digital voltmeter when the beam from a small 3 mw helium-neon laser fell (a) full on the detector and (b) after scattering by passing through a 3 x 5 paper index card. The observed deflection on the digital voltmeter went from 3 V to 0.10 mV; thus if full on is 3 mw, then the scattered beam was 100 nanowatts. This is still about two orders of magnitude above Johnson noise levels.

The flow rates of gases (He , O_2 , and CS_2) were determined using Fisher and Porter Precision Bore Flowrater Tubes and calibration curves supplied by the manufacturer. The pressure of each gas was monitored by a gauge in the line between the gas inlet and the valve leading to the vacuum system.

Either Mallinckrodt or Baker reagent grade CS_2 was used directly from the vendor's bottles. Helium and oxygen were used directly from commercial cylinders without further treatment.

Each reaction tube in this study was provided with an arm for attachment of a Wallace and Tiernan (Model FA 160) absolute pressure gauge.

Alignment of the Laser Cavity: - One of the most important steps necessary for successful laser operation is alignment of the optical cavity and detector. Thus, prior to each experiment, alignment must be checked.

First the reaction tube is pumped down to the pressure which corresponds to its normal operating pressure. As shown in Figure 4, the beam from a He-Ne laser is coupled to the experimental laser cavity by means of a glass slide which is mounted on a translation stage which can accurately position the slide. The cavity mirrors are then adjusted so that all the spots on the mirrors, windows, and glass slide are in line. This is seen to be the case when spots on any one surface from different numbers of passes through the cavity fall on top of one another. It is also noted that the alignment laser beam has been properly coupled to the cavity when the reflected spot from the glass slide due to previous reflections in the cavity falls directly on the output window of the alignment laser.

The detector is then aligned with reflected light from one of the Brewster windows until the output signal caused by the alignment laser is at a maximum. Until recently this completed the alignment procedure. However, when the experiment was performed, this alignment proved not to be perfect and some further minor adjustments of the mirrors had to be made. It had been noticed, though, that certain alignments of the laser cavity and detector produced very erratic detector output for the alignment laser signal. Also, it was recently noted that when this effect occurred the alignment was perfect for the experimental chemical laser output. Further investigation showed this effect to be produced by interference in the light beam reaching the detector. This interference seems to be caused by the lack of long-time coherency which is typical of all lasers. That is, lasers possess excellent spacial coherency but poor time coherency (35). Thus, light reaching the

detector after one pass through the laser cavity will not be in phase with light that passed through the cavity two or more times before reaching the detector. The net result is constructive and destructive interference in the light reaching the detector. Now after the above alignment steps are completed, an additional fine tuning of the mirrors is performed to produce maximum interference (erratic) output from the detector. No further adjustments are needed during the experiment. Following these procedures the glass slide (used to couple the He-Ne laser beam to the experimental laser cavity) is moved out of the cavity by means of the transverse stage.

Reactant Flow: - Air is removed from the CS₂ reservoir by opening the stopcock and allowing the insuing CS₂ vapor to purge the air throughout the apparatus (see Figure 6). The stopcock is then closed, and the CS₂ flow control needle valve is also closed. This procedure is performed to check for leaks in the CS₂ delivery system. Very small leaks, such as a poorly greased ground glass joint, can greatly reduce or destroy lasing. It is interesting to note that similar leaks in the O₂ - He delivery system produce only small effects on laser output.

While the CS₂ delivery system is being leak checked, the O₂ and He flows are established and adjusted to those flow rates which have been previously shown to produce maximum lasing. If it is established that the CS₂ delivery system is leak-tight, then the high-voltage transformers for the two Woods tubes are turned on, and discharges are established in each tube.

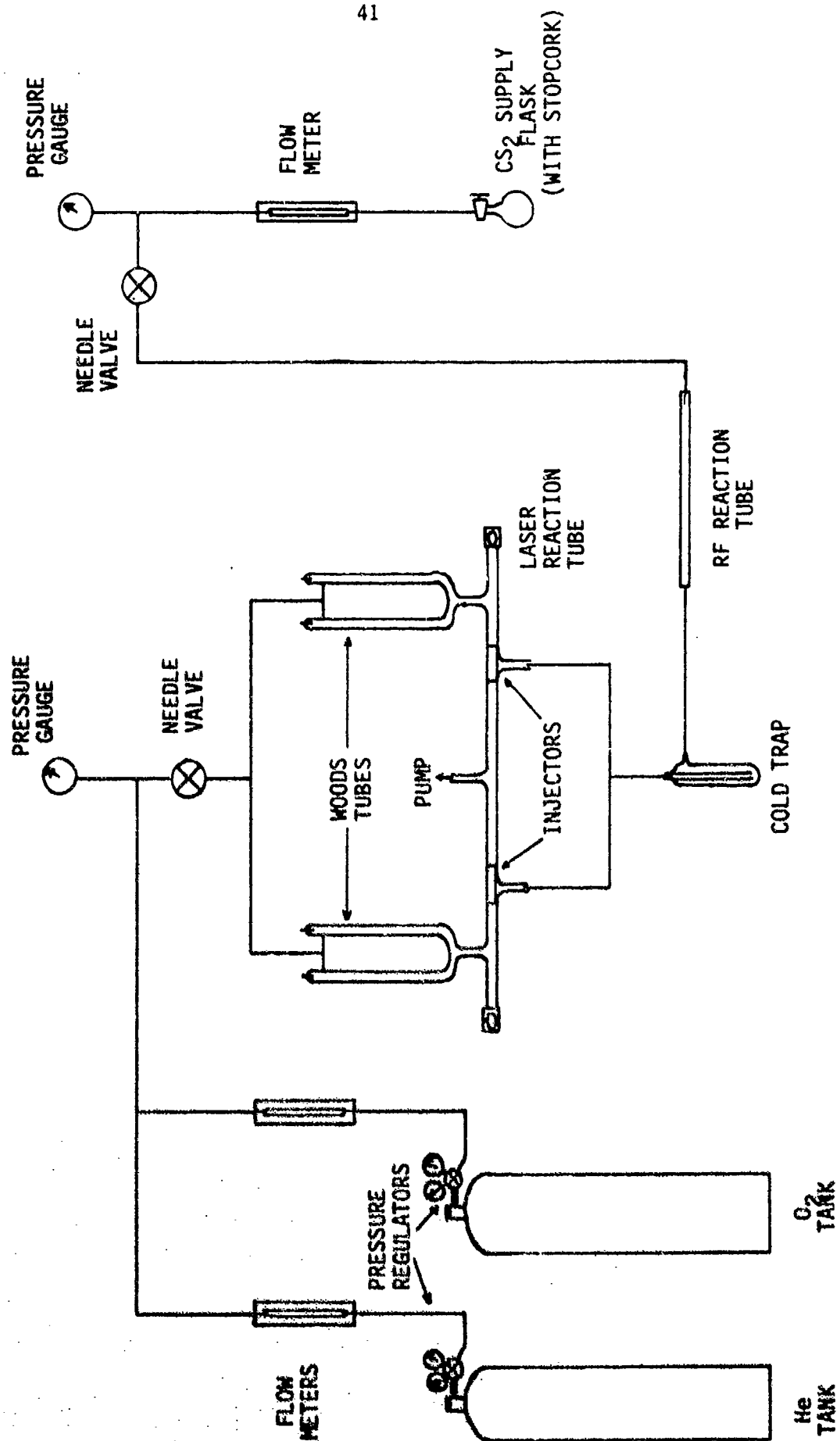


Figure 6. Schematic diagram of reactant flow paths.

Finally, then, the stopcock between the CS_2 flask and delivery system is opened. The CS_2 control needle valve is then opened slowly and the CS_2 flow is adjusted for maximum cw laser output.

Experiments Using Radio Frequency Discharge: - When the RF discharge is to be used, the generator is turned on and the radiation is tuned to the RF reaction tube prior to the opening of the CS_2 supply stopcock. Before the reaction tube is exposed to CS_2 the discharge can be established and the generator matched to the discharge quickly. This is important in that it reduces harmful screen and grid dissipation in the RF power amplifier tube. The RF generator is then turned off, and the lasing is established and tuned for maximum cw output. After it is established that all systems are working properly, the CS_2 supply is turned off, and the RF generator is turned on. The CS_2 supply is then re-established and tuned for maximum lasing. Now, while the system is lasing and the RF discharge is operating, a cold finger trap located in the CS_2 supply line between the RF reaction tube and the laser reaction tube is chilled to -120°C using a 2-methylpentane-isopentane mixture. This trap will condense the undissociated CS_2 while not impeding the flow of the CS. Further adjustments of the CS_2 and oxygen flow rates are then made in attempts to obtain pure CS fueled lasing.

A similar procedure is followed when using either the 60 Hz discharge reactor or the hot tungsten filaments for CS production.

Results

As in the case with all chemical lasers, lasing occurred at several wavelengths. The most prominent lines were at $5.33\ \mu\text{m}$ and $5.40\ \mu\text{m}$ which is in agreement with results of other experimentors (36).

Lasing output was stable, probably in part because the double-reactor configuration put both windows upstream of the sulfur-producing reaction thus eliminating sulfur deposition on the windows. The character of the laser emission is revealed by the low dispersion spectral trace of Figure 7, and it is in agreement with earlier observations as regards the particular transitions and relative strengths. At slit widths of 0.3 to 0.9 cm, several bands were observed. The maxima of the most intense and stable bands occurred at 5.33 μm and 5.40 μm , as was the case with Wittig (5.33 μm and 5.39 μm) (36). Wittig observed two additional, much less intense bands at 5.26 μm and 5.50 μm . We also see two weaker bands at 5.24 μm and 5.47 μm . The total output power available through the 1 mm hole in the flat mirror as a function of CS_2 flow rate through the laser was determined using the Jodan power meter (model PM-550). These data are plotted in Figure 8, and the maximum power was found to be 8 mw which occurred at flow rates of 2.3×10^{-3} mole/sec O_2 , 4.8×10^{-3} mole/sec He, and 2.5×10^{-4} mole/sec CS_2 . This maximum power represents then an overall chemical efficiency of somewhat less than 0.1 percent. As shown in Figure 9 fluctuations of about 3 percent in the output power were observed. The majority of this is probably due to fluctuations in the CS_2 flow rate.

Under certain conditions the lasing was observed to be pulsed by the 60 Hz high voltage discharge used to produce the atomic oxygen. When using the RF discharge to produce atomic oxygen, this ripple disappeared. This ripple effect is most prominent under non-stoichiometric conditions, and, as is shown in Figure 10, it produces two peaks in pulsed lasing output which bracket the peak in continuous wave lasing. We believe that the high voltage discharge is exciting available ground state CO and thus

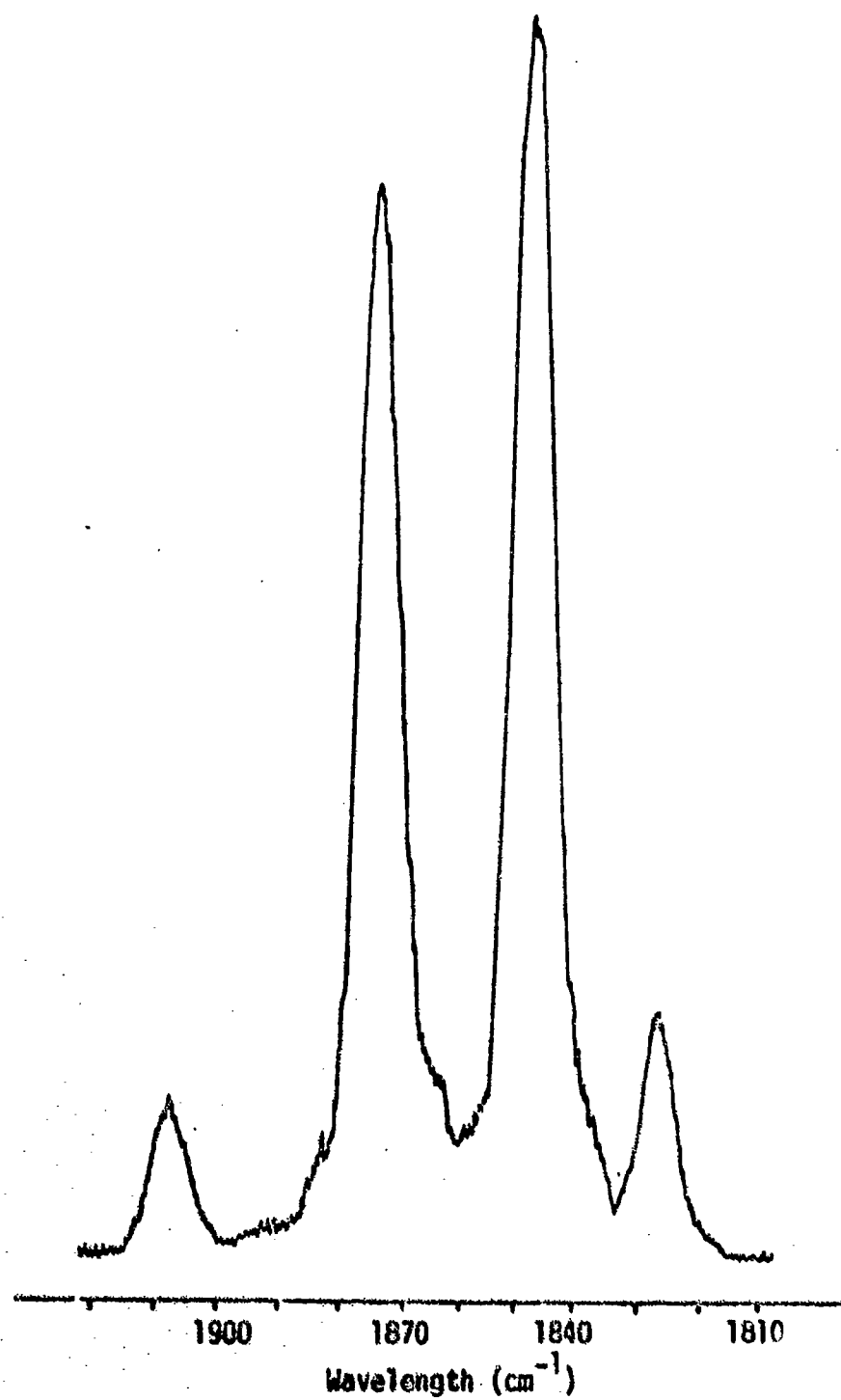


Figure 7. Frequency distribution of CO chemical laser output.

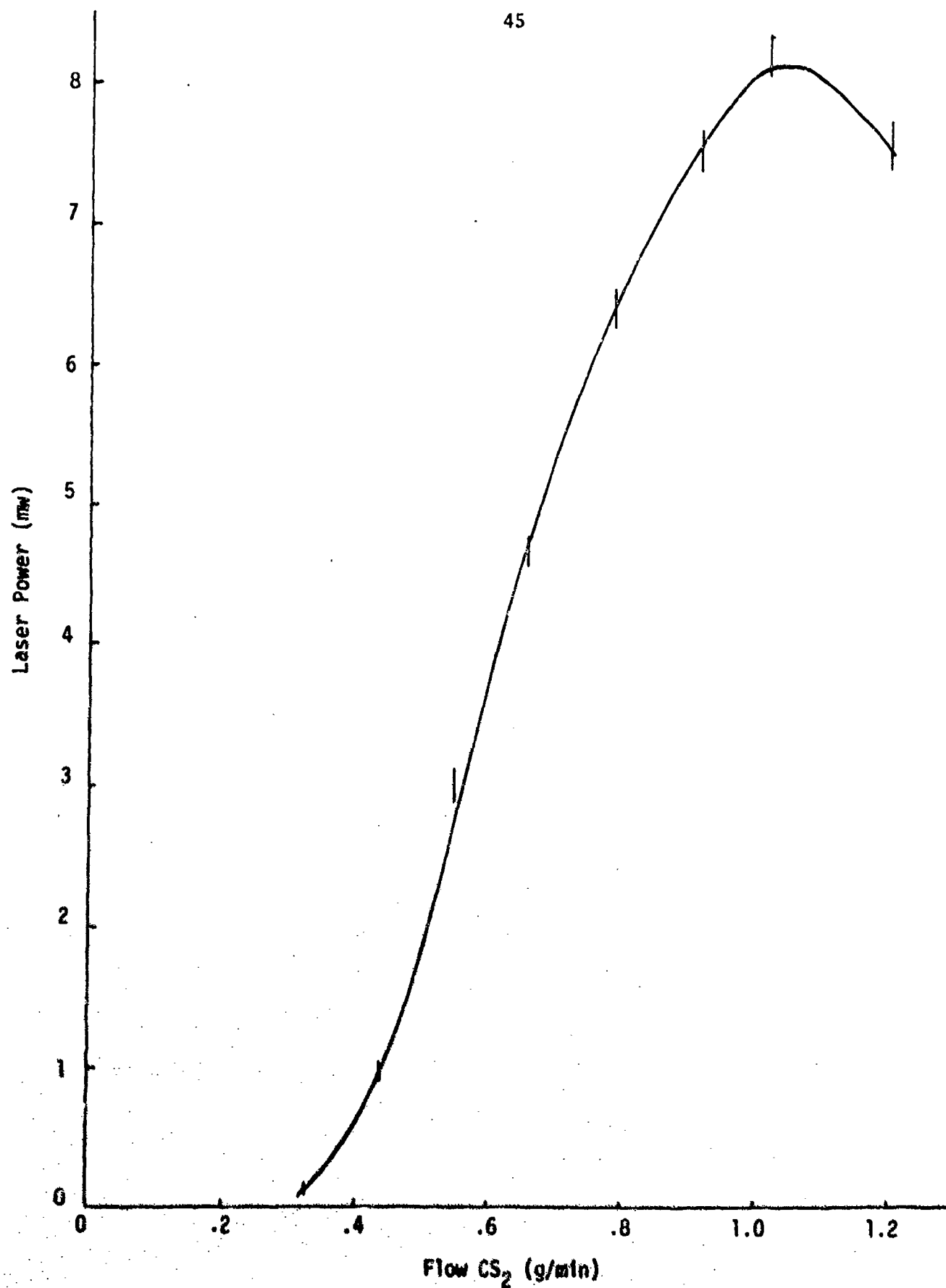


Figure 8. Profile of laser output power versus CS₂ flow rate.

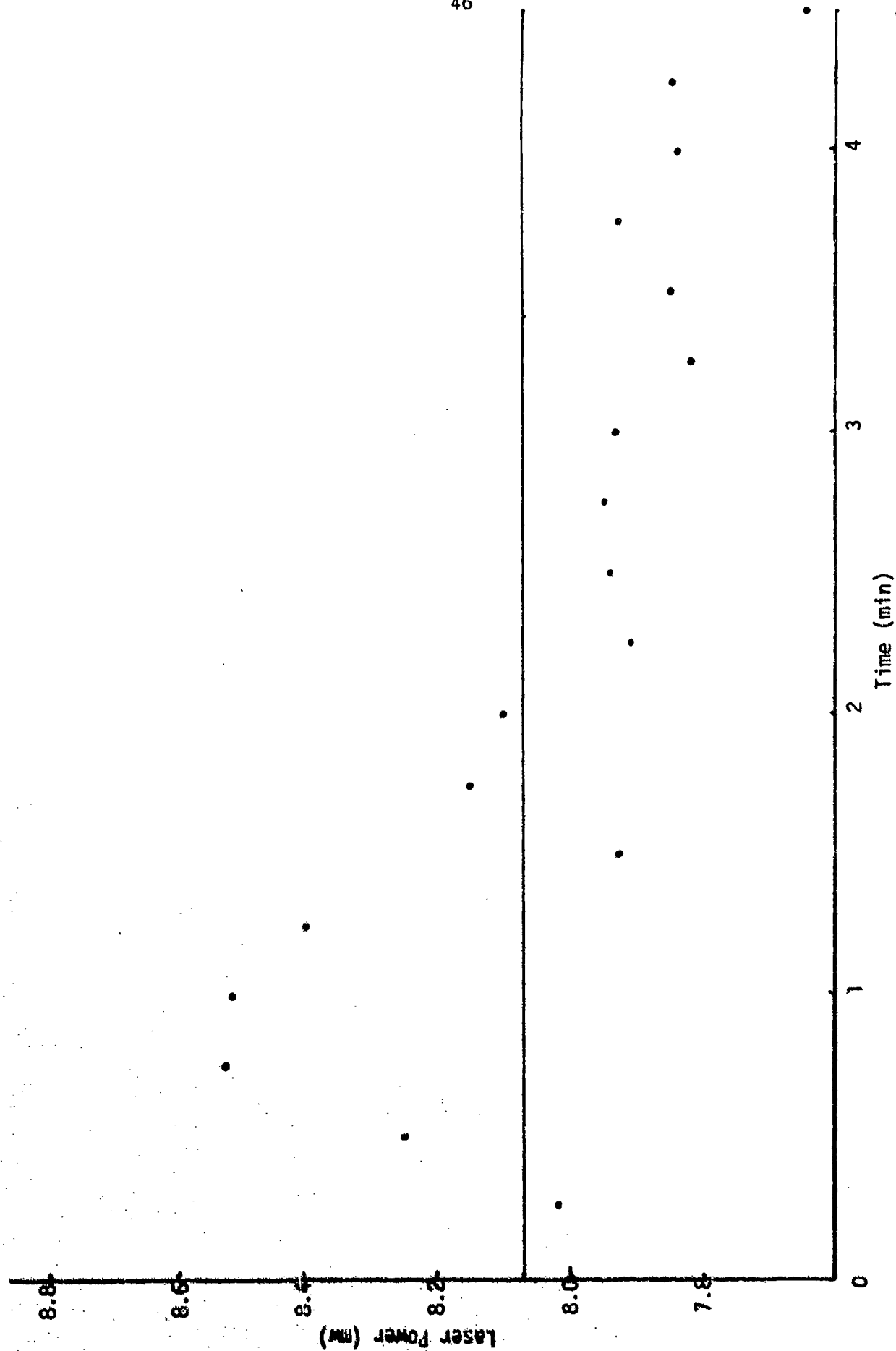


Figure 9. Variation of laser power over a short period of time. Horizontal line represents the average power.

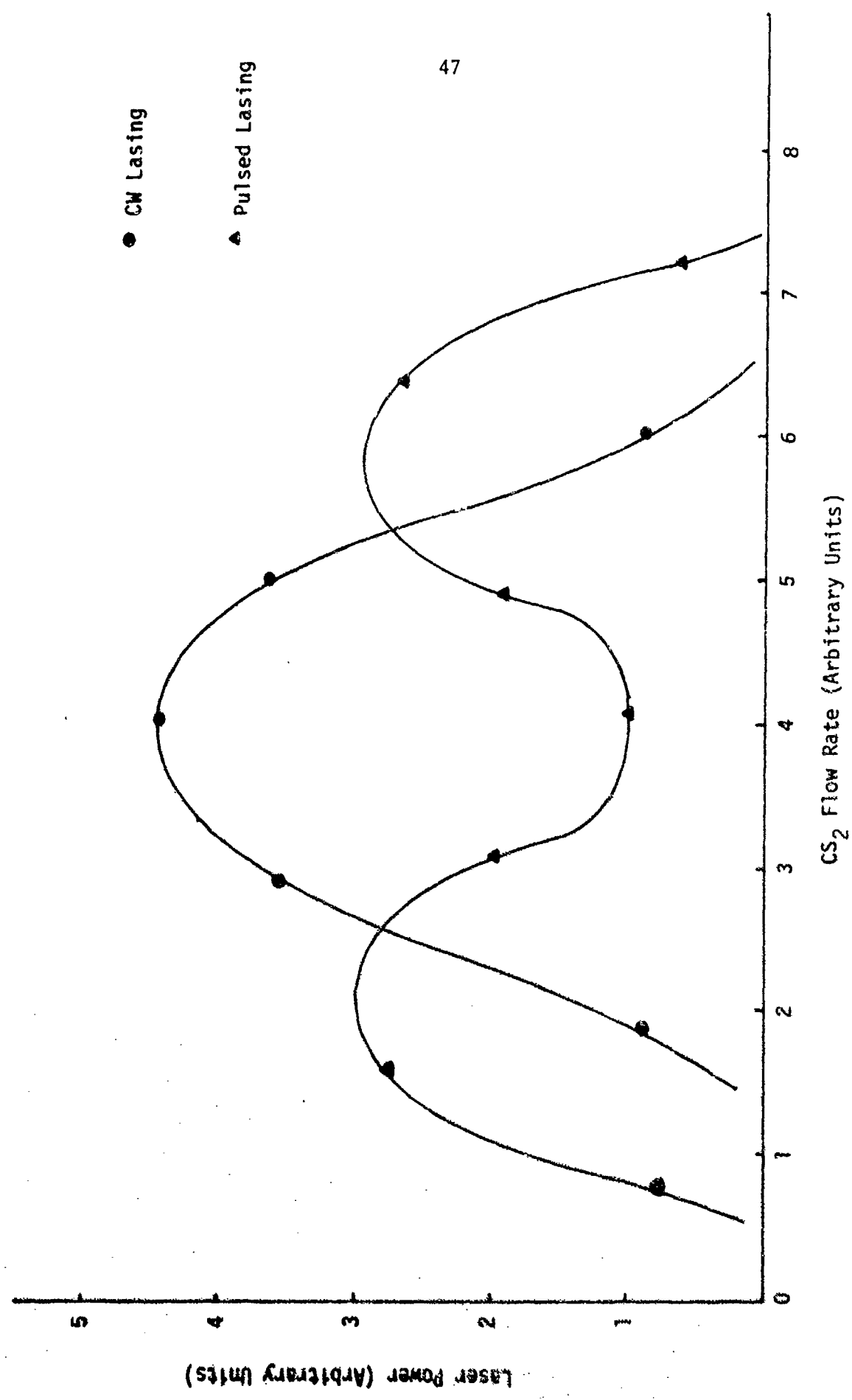


Figure 10. Profiles of CW and Pulsed Lasing.

enhancing the population inversion, which has been then only partially produced by chemical pumping. Thus, when cw lasing is at a maximum, the availability of unexcited CO is reduced, and consequently, the pulsed lasing is reduced creating the dip in pulsed lasing between the two maxima.

As stated earlier, the initial unique goal of this project was to produce lasing fueled by pure CS and to study the properties of this lasing. However, it now seems as though lasing fueled by pure CS will not be achieved, and the reasons for this should be exposed.

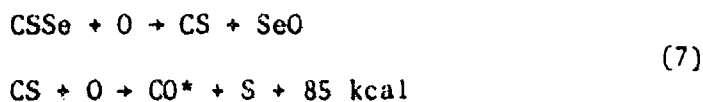
First among these reasons is the inability to store CS for later use. Though CS can be produced and deposited as a pure white solid in a suitable cryogenic cold trap, attempts to warm this trap to release the CS always resulted in violent explosions which completely destroyed the CS (not to mention the apparatus). For this reason CS has to be used immediately after production in some type of continuous flow system. However to achieve lasing rather high flow rates of CS are required, and at these rates it is very difficult to maintain an electrical discharge necessary to produce the CS. As it turns out, the amount of energy needed just to maintain the discharge at these high flow rates is sufficient to reduce the flowing CS_2 and CS to carbon and sulfur. The results are heavy wall deposits of carbon and sulphur and little production of CS. The wall deposits demonstrate that there is a reduced supply of CS_2 to the laser, and as would be expected the laser output is also reduced. These same problems existed for RF, 60 Hz discharge and hot filament methods of CS production. Sufficient CS was

produced and did survive passage through the trap at -130°C that condensed the undissociated CS_2 to yield a small soft blue flame in the laser reactor. The concentration was insufficient to produce the bright cone that was observed when feeding CS_2 alone, and lasing was never observed.

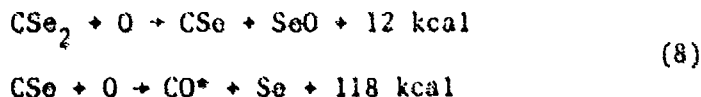
During some experiments in which the radio frequency discharge was used to produce CS, a liquid nitrogen trap was in the vacuum line immediately preceding the pump to remove sulfur produced by the lasing reaction. At the end of the experiment, this stainless steel trap was isolated from the system and opened to the air. Shortly thereafter, an explosion occurred in the trap, indicating that CS had been produced by the RF discharge, survived flow through the laser reactor only to be frozen out in the trap. The liquid nitrogen trap was omitted in some CS experiments so that the unreacted CS went directly through the pump. But the penalty is that free sulphur will also go into the pump causing it to finally jam.

CSe SYSTEM

We also wish to react either CSSe or CSe₂ with atomic oxygen to produce vibrationally excited CO, as in the case of the analogous reaction of O with CS₂. In the case of CSSe, the C-Se bond is weaker than that of C-S; and hence we expect reaction according to the following scheme:



In the case of CSe₂, we expect:



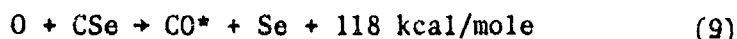
In addition to burning CSSe, this compound may prove to be a good source of pure CS without going to the exceedingly high temperatures required to pyrolyze CS₂. Thermodynamic calculations reveal that the equilibrium dissociation of CS₂ yields essentially pure CS near 2400 K and pressures of 10-20 torr. CSSe is unstable near 800°C, and it is expected to crack to form CS and Se. Se can be easily removed by cold trapping (along with any unpyrolyzed starting material), and the remaining pure CS can be reacted with atomic oxygen in the usual way in the optical cavity.

We have produced CSSe and CSe₂ by evaporating selenium at 400-500°C into a stream of CS₂ at the entrance end of a pyrolysis tube (37). The gaseous mixture reacts near 750°C producing the selenium compounds, which are collected by condensation and separated by distillation. The composition and purity of the distillates are monitored by infrared spectra. The

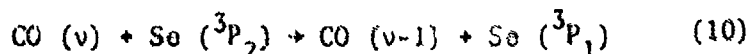
yield was poor. A second technique (38) was used in which CH_2Cl_2 was passed over molten selenium at 500°C , followed by condensation and purification of the products as described above. Again the yield was poor with only about 1 percent of the CH_2Cl_2 appearing as CSe_2 .

The CSe_2 has been burned with O, O_2 , He mixtures at flow rates and at stoichiometric ratios similar to those that routinely result in strong CO lasing from the combustion of CS_2 , but no lasing has been observed. A heavy deposit of Se rapidly coats the walls of the reactor between the teflon injectors.

We are as yet unable to clearly explain this lack of lasing, particularly since lasing has been reported in the flash initiated reaction (39). In these earlier studies, O atoms were photolytically produced from SO_2 and CSe was simultaneously produced from CSe_2 . Infrared emission from CO to $v=20$ was observed consistent with



which is rather more exothermic than is the reaction of CS with O where the heat of reaction is only 85 kcal/mole. Both reactions supposedly deposit about 85 percent of this exothermicity in the vibrational energy of the CO product (40). Power levels were about the same with CS_2 and CSe_2 , but in CS_2 bands from (14, 13) to (3, 2) were observed while in CSe_2 bands from (20, 19) to (9, 8) appeared. The lower levels of CO in the CSe_2 experiments were probably quenched by



which is near resonant at $v=7$. This would enhance inversion of the higher levels.

The electric discharge initiated pulsed reaction of CSe_2 and O_2 also yielded lasing on the (18, 17) to (7, 6) transitions (41).

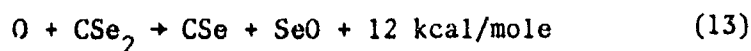
Our tentative explanation of the lack of success with continuous wave lasing is due to the effect of the fast reaction,



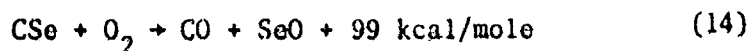
with CS_2 which is exothermic by 6 kcal/mole vs. the slow reaction of



with CSe_2 which is endothermic by some 19 kcal/mole. Thus with CS, every reaction with an O atom will produce an S atom which in turn rapidly produces another O atom from O_2 . This replenishment of O atoms does not occur when burning CSe, and evidently all of the oxygen atoms are used up in the production of CSe in the first place,



Flash initiated studies of CSe_2 and O_2 where only CSe is formed failed to produce lasing indicating that the reaction,



is unimportant in producing CO^* as it is also with CS. Similar flash experiments with CS_2 , O_2 mixtures does produce lasing from



To overcome this difficulty, we are exploring the possible production of CSe from the external discharge or pyrolysis of CSe_2 before it enters the laser reactor. CSe_2 is unstable near 800°C . Perhaps CSe will be as long lived as is CS which is indefinitely stable as long as the solid CS is maintained at liquid air temperatures.

CRYOGENIC LASER

We selected O_2F_2 as the first high powered cryogenic oxidizer to be studied as regards its effectiveness in pumping population inversions. Dioxygen difluoride is a powerful oxidizer that may be synthesized from an electric discharge in the mixed elements in which the discharge tube reactor is immersed in liquid oxygen (90K). The yellow liquid at 90 K must be kept cold, for it decomposes back into the elements at dry ice temperature, $-80^{\circ}C$, at a rate of about 4 percent per day.

O_2F_2 was first reported in 1933 as formed from a discharge in the mixed elements at 10-20 torr and with the discharge tube reactor immersed in liquid air (42). It is an orange-yellow solid, melting at 199.7 K to form an orange-red liquid that decomposes rapidly and exothermically near its boiling point of 216 K at which temperature, it rapidly and exothermically decomposes back into F_2 and O_2 . Its heat of formation is 4.7 kcal/mole (43), and microwave spectra (44) reveal it to be a non-planar chain molecule similar to hydrogen peroxide except for its extraordinarily long O-F bond of 1.58 Å and short O-O band of 1.22 Å equivalent to that of molecular oxygen at 1.21 Å. O_2F_2 solutions in Freon 13 ($CClF_3$) exhibit an epr signal from the O_2F radical from which one deduces radical concentrations in solution of up to 0.5 percent (45). This molecule was the first example of a species stable only at very low temperatures that has been observed by mass spectrometric techniques (46). There is no parent ion in either the positive or negative ion spectra, the principle ions are O_2F^+ (100) and OF^+ (10), but other probable ions were masked by the decomposition of the O_2F_2 in the ion source. The appearance potentials of these two ions, $A(O_2F^+) = 14.0 \pm 0.1$ eV and $A(OF^+) = 17.5 \pm 0.2$ eV, permit the development of the molecular energetics of O_2F_2 (46).

$$D(F - O_2F) = 0.8 \text{ eV}$$

$$D(FO - OF) = 4.5 \pm 0.2 \text{ eV}$$

$$D(O_2 - F) = 0.8 \text{ eV}$$

$$D(O - OF) = 4.8 \text{ eV}$$

The O-F bond energy of 18 kcal/mole is half that of F_2 at 37 kcal/mole and is substantially less than C-F (107 kcal/mole), S-F (68 kcal/mole), N-F (65 kcal/mole), Cl-F (60 kcal/mole) or I-F (46 kcal/mole). F_2O_2 is very unlike H_2O_2 , for in the fluoride, the bond distance between the oxygen atoms is about the same as that in molecular oxygen.

The O_2F radical has been proposed as an intermediate in the oxygen-inhibited reaction of H_2 and F_2 (47).

We have routinely synthesized O_2F_2 in a 5 cm ID reactor with 1.5 cm OD electrodes mounted 6 cm apart, using a discharge current of 25-75 ma in the mixed elements at 18-25 torr, and with the reactor immersed in liquid oxygen at 90 K.

The vapor pressure of O_2F_2 is given by the equation (48)

$$\log P = 7.515 - (1000/T) \quad (16)$$

and its rate of decomposition by the equation (49)

$$-\frac{d(O_2F_2)}{dt} = (O_2F_2) \times 10^{12.4 - (17,000/4.57T)} \quad (17)$$

Thus, at 195 K (dry ice temperature) its rate of decomposition is 4.3 percent per day. Since the temperatures (133 K - 161 K) required to produce a vapor pressure of O_2F_2 sufficient for use in a chemical laser

(1-20 torr) are considerably lower than dry ice temperature, the amount of decomposition of O_2F_2 prior to reaction in the laser cavity should be negligible.

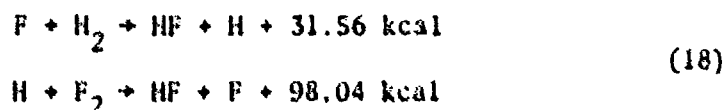
Small O_2F_2 , H_2 Laser System - To gain insight into the operating

peculiarities of this unusual system as an aid in the design of the reactor portion of the full-scale unit, we have built the test device shown in Figure 11. This unit is essentially an adaptation of the design of the dual head-on longitudinal reactor used in the studies with CS and O. This latter design has been modified by replacing the Teflon injectors with a pair of copper injectors internal to two massive copper cold fingers which extend downward from the bottom of a brass Dewar vessel. In operation, this Dewar is mounted above the glass laser tube, so that the cold fingers extend down into a pair of matching wells built into the laser tube. The O_2F_2 reservoir is immersed in the refrigerant in the Dewar, and the oxidizer itself is transferred to the injectors through 1/4 inch copper tubing. This arrangement allows injection of O_2F_2 over a temperature range of 90 K to 173 K, depending on the refrigerant contained in the brass Dewar.

The O_2F_2 synthesis reactor also serves as a reservoir for O_2F_2 , and by bubbling pre-cooled He through the liquid O_2F_2 , the oxidizer is swept into the laser reaction chamber through the injectors in the copper cold fingers. The system has been designed so that the fuel gas, H_2 , after first being pre-cooled by passing through the refrigerant in the brass Dewar, also enters the laser reaction chamber through the same cold fingers, but by means of a separate set of injector holes.

The system functions well with H_2 and F_2 where the opposed flame jets can burn indefinitely with liquid nitrogen in the cryostat. Satisfactory tests with O_2F_2 and H_2 have not yet occurred, but the problems seem to be purely technical in nature. We have constructed and tested several devices rather like that shown schematically in Figure 11. There were several ill-fated designs of all-glass construction, but the thermal stresses proved too severe. The present all-metal system seems to offer the best potential for success, and work is continuing.

O_2F_2 as a Fluorine Source for the HF Chemical Laser - The pumping reactions which lead to a vibrational population inversion with subsequent laser emission from the HF molecule are:



Although the second of these reactions has the greater exothermicity, the first reaction is more efficient in the production of vibrationally excited HF molecules. It has been estimated that for the first reaction, 22.6 kcal is liberated in the form of vibrationally excited HF (72% efficiency), while for the second reaction the comparable value is 43.1 kcal (44% efficiency).

A great variety of HF chemical lasers have been constructed differing principally in one or more of the following aspects:

1. Chemical nature of the F atom source. Among the molecules that have been utilized are F_2 , SP_6 , UF_6 .

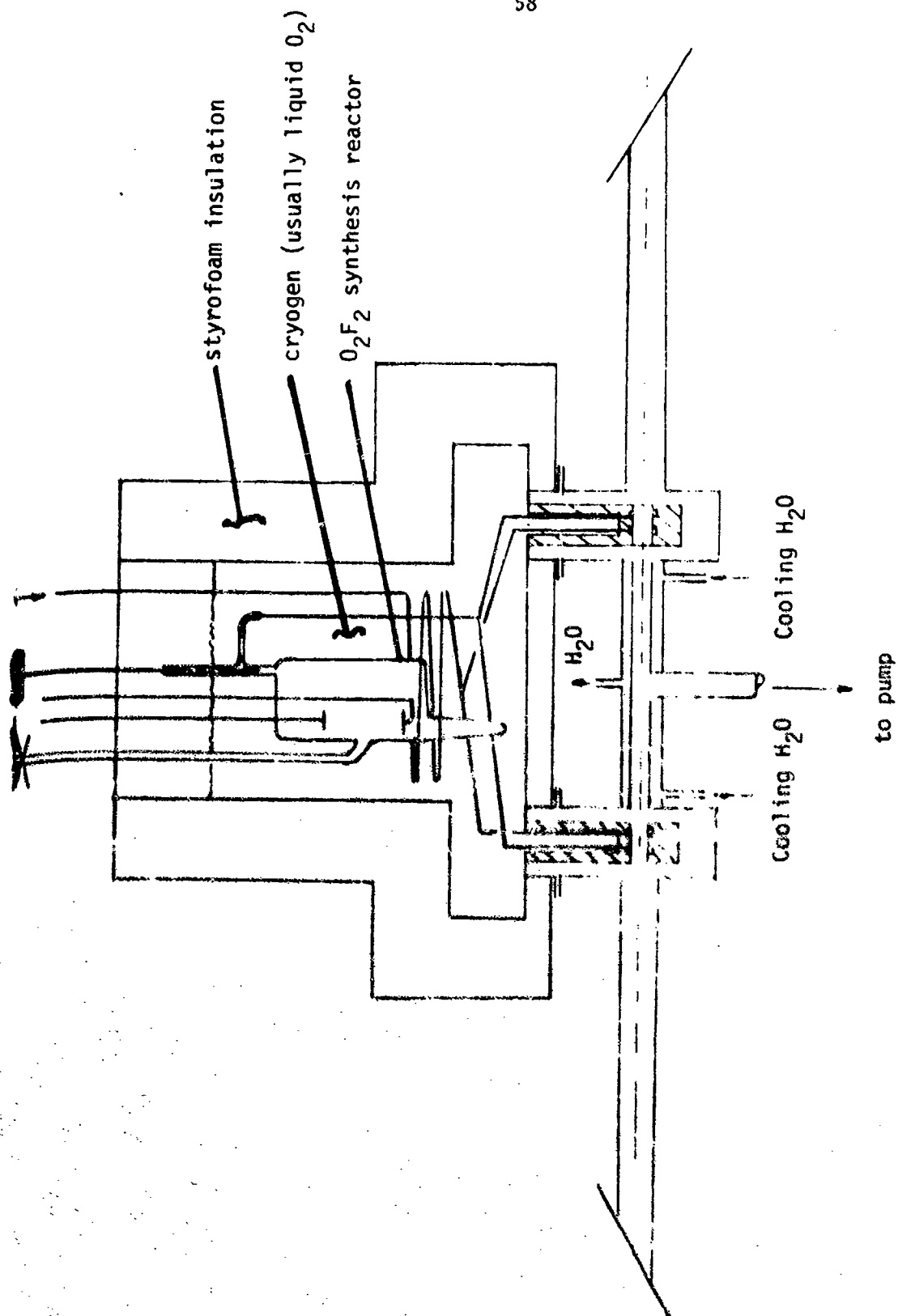


Figure 11. Schematic of cryogenic laser facility.

MoF_6 , XeF_4 , ClF , ClF_3 , IF_5 , NF_3 , N_2F_4 , and CF_4 and lower fluorinated methanes, CCl_2F_2 , and various other F or (Cl and F) substituted methanes and ethanes.

2. Chemical nature of the H atom source. Among the molecules utilized are H_2 (or D_2), CH_4 , C_2H_6 , C_3H_8 , HCl , HI , CH_3CN , NH_3 , and various other F, Cl, Br or I substituted methanes and ethanes.
3. Method of production of F (or H) atoms. Resulting lasers include flash and electrically initiated pulsed lasers, electrical discharge CW lasers and purely chemical CW lasers.
4. Orientation of molecular flow axis relative to optical axis has utilized both longitudinal configurations (axes parallel) and transverse configurations (axes perpendicular). Of these two configurations, the transverse configuration is best suited for higher power lasers.

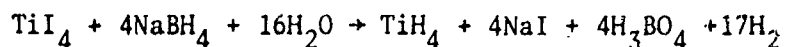
In contrast and with this as background, we are attempting to burn O_2F_2 with a variety of fuels or hydrogen donors in our optical cavity systems in an attempt to broadly screen possible systems in a search for high power efficiencies.

TiH_4 as a Hydrogen Donor in the HF Laser - We also sought to prepare relatively large amounts (i.e., 5-10 gas) of TiH_4 for use as a fuel in the HF laser. One might tentatively assume the bond energy of TiH_4 to

be about equivalent to that of GeH_4 and SnH_4 . The infrared spectrum however reveals TiH_4 to have a weaker bond than either with a calculated bond distance of 2.1 \AA which may be compared with 1.48 \AA and 1.76 \AA in GeH_4 and SnH_4 , respectively. The molecule is a spherical top with tetrahedral symmetry. The synthesis of TiH_4 , in low yield (about 0.1 percent) from the reaction of TiI_4 with NaBH_4 in toluene and water was first reported by Thomas and Baker (50). We attempted to modify their procedure in the hope of obtaining increased yields.

A 500 cm^3 three-necked flask served as the reactor, and this was connected to a two-trap system containing first a toluene slush at -95°C to condense the solvent that evaporated from the reactor followed by liquid nitrogen at -196°C to condense the TiH_4 product. One of the reactants (TiI_4 in toluene) was slowly added dropwise to the reaction vessel using a 500 cm^3 pressure equalized separatory funnel. The reaction was conducted at pressures of 300-400 torr. A typical preparative run involved 28 gm of TiI_4 (0.05 moles) in 225 cm^3 of toluene and 7.6 gms of NaBH_4 (0.2 moles) in 50 ml of water. The reaction occurs at the interface between the two immiscible solvents. This is an unusual synthetic approach, but a necessary one in this case since TiI_4 reacts with water and the NaBH_4 needs water to react at all. The mixture was stirred continuously to maximize the interfacial surface area, and the reaction vessel was immersed in an ice bath. The reaction was vigorous and the addition of TiI_4 had to be carefully controlled in order to prevent excessive foaming and too rapid evolution of gas.

Apparently, there was a large amount of free hydrogen produced in keeping with the stoichiometric equation,



The gaseous product was collected at -196°C and pressure and volume measurements suggested that about 0.14 gm of TiH_4 had been produced, and thus the yield was approximately 5 percent. This was however an insufficient sample to give a clear reading of the infrared spectrum using a small Perkin Elmer model 337 infrared spectrophotometer with a gas cell of 10 cm^3 volume with KBr windows. The scan was from $400\text{--}4000\text{ cm}^{-1}$.

The analysis of this material is being carried out by comparison of its infrared spectrum with the spectrum of the pure material, as reported by Thomas and Baker. Some difficulty has arisen in the procedure due to apparent decomposition of TiH_4 at room temperature in our metal ir gas cell. We expect to overcome this difficulty by the use of a glass-bodied gas cell (51).

From the point of view of laser operation and efficiency, a very labile hydrogen donor such as TiH_4 is exciting, but from the view of handling the reagent, this very same property now makes for difficulties. However, Thomas and Baker did report the infrared spectrum of the gas to be unchanged on standing two hours at room temperature in their gas cell. Titanium tetrahydride is purportedly reasonably stable at room temperature, but on moderate warming, it decomposes to deposit a titanium mirror on surfaces. We proposed to burn TiH_4 with O_2F_2 in our laser facility. Unfortunately these experiments have not yet been performed, however work is continuing, and the results will be communicated to AFOSR as soon as possible.

Large Laser Facility - A large laser facility utilizing the transverse configuration and versatile enough to allow the burning of a wide variety of fuels and oxidants, including these unusual cryo-reagents, has been designed. In the description that follows, the use of O_2F_2 is predominantly mentioned. This is merely a rhetorical convenience, for the facility has been designed to conveniently handle any labile compounds. As shown diagrammatically in Figure 12 and 13, this facility is built on two levels of our building with a large mechanical vacuum pump on the lower level and with the laser proper along with associated heat exchangers and low temperature traps occupying the upper level.

The system has been designed to use interchangeably either a 250 cfm or a 750 cfm mechanical pump both manufactured by Beach-Russ. These pumps were placed on loan to this project at no cost by the VPI & SU Department of Aerospace Engineering. Two sections of flexible Teflon bellows have been placed between the intake of the mechanical pump and the cold trap section of the vacuum line to minimize the transmission of vibration from the pump to the laser optical cavity and the externally mounted mirrors.

The cold trapping section, consisting of a pair of butterfly valves, a water cooled chevron baffle, and a liquid nitrogen cooled chevron baffle, and all upstream components of the system are of stainless steel construction, because of the corrosive nature of the HF , O_2F_2 , F_2 , etc. that are to be handled in the system. A five foot section of water cooled vacuum line located immediately downstream of the laser serves as a heat exchanger to reduce the temperature of the hot exhaust gases before they reach the

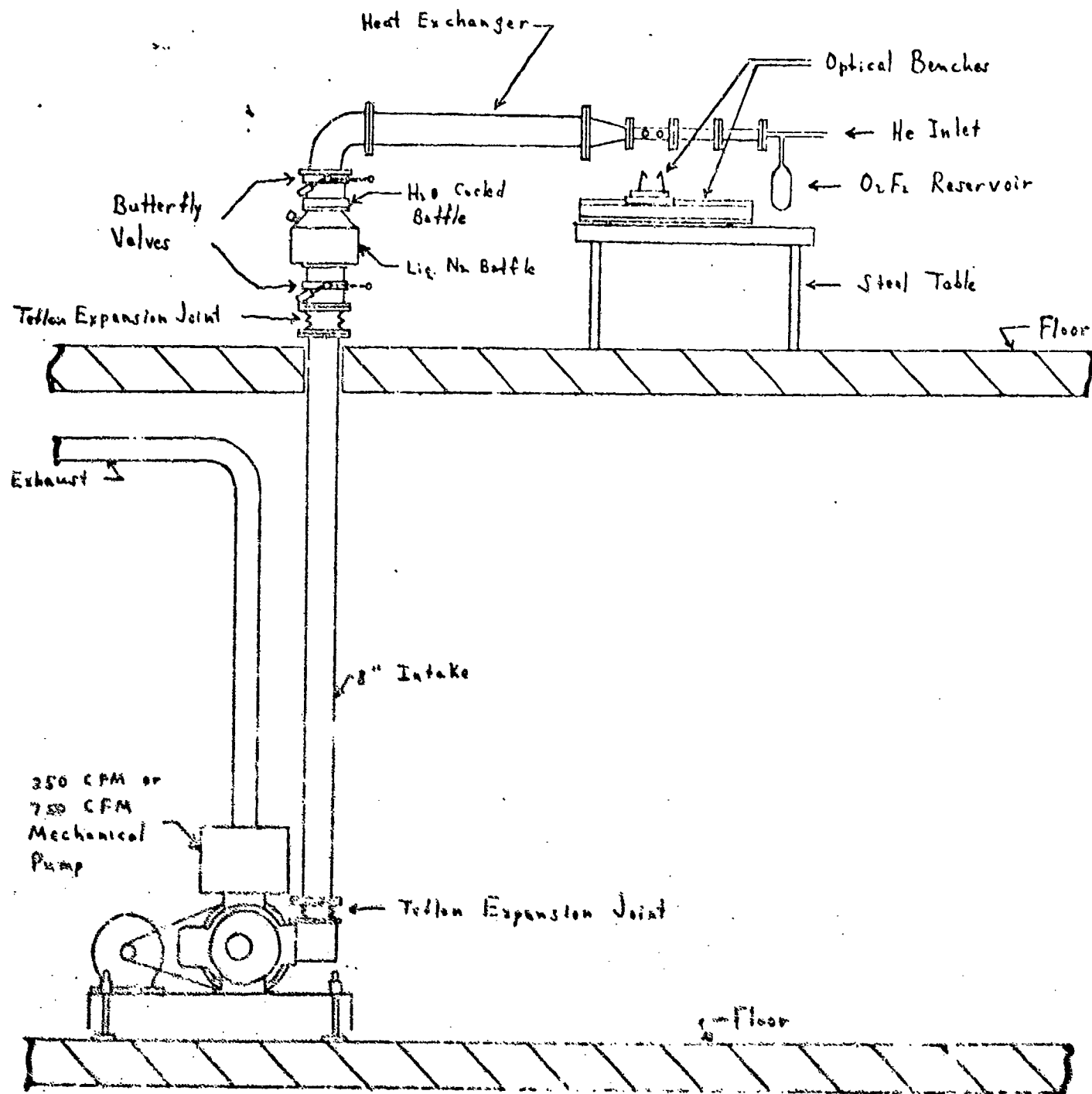


Figure 12. Elevation of layout of transverse laser facility.

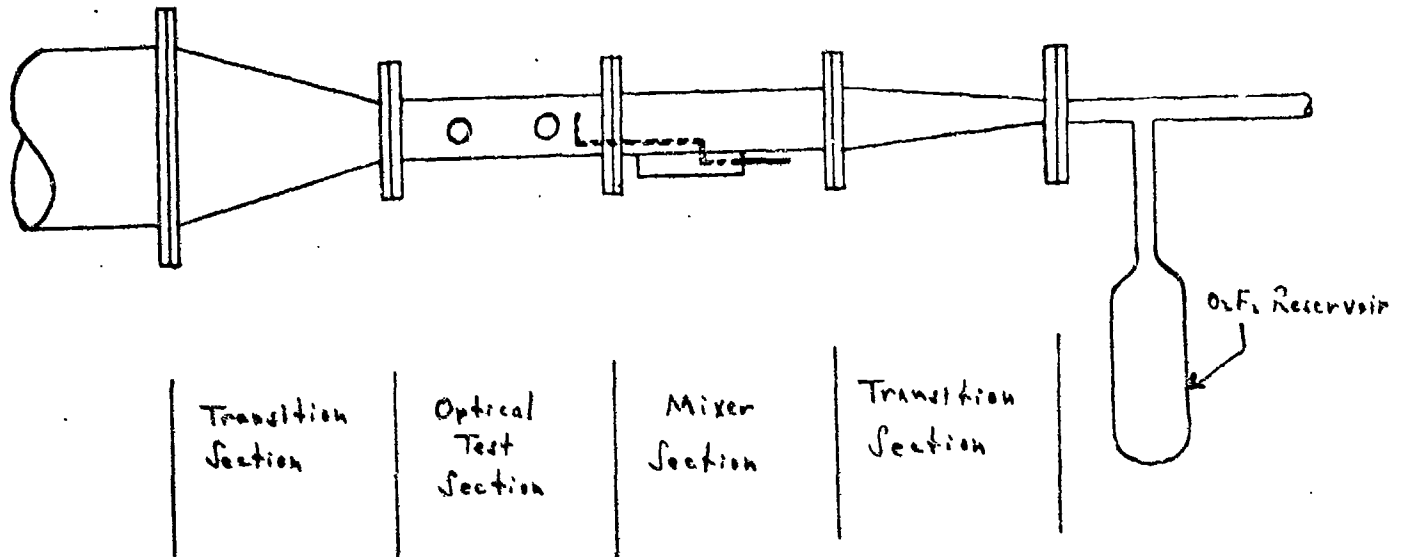
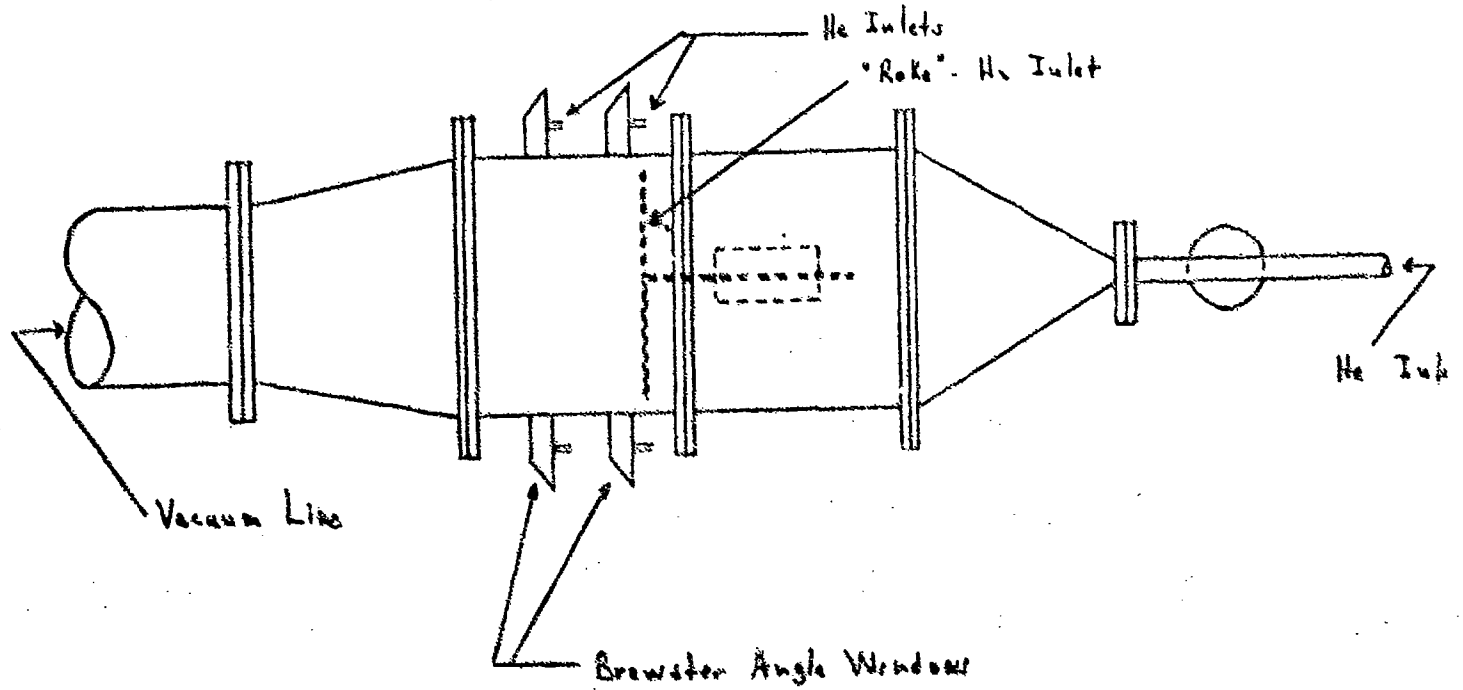
Side ViewTop View

Figure 13. Transverse laser, conceptual design.

cold trap section. After completion of a run, the corrosive gases trapped at liquid nitrogen temperature can be removed by allowing the cold trap section to warm up followed by the pumping of the released gases by means of a small auxiliary vacuum pump through a scrubber containing a solution of caustic. Cold trapping was chosen over other possible methods of handling the corrosive reaction product gases for convenience and because the cryogenic pumping effect considerably increases the pumping capacity of the system.

The laser proper consists of two transition sections, a mixer section and an optical test section. Because of the thermal instability of O_2F_2 , provision is made for cooling the O_2F_2 inlet, the upstream transition section, and the mixer section to cryogenic temperatures. The optical test section, within which the reaction occurs, and the downstream transition section are provided with water cooling. O_2F_2 or a mixture of O_2F_2 and He, enters the laser through the O_2F_2 inlet and moves downstream through the first transition section and into the mixer section. H_2 is injected at right angles into the O_2F_2 flow in the mixer section through an array of injectors which resembles a rake. Each of the tines of the rake, which is made of stainless steel tubing, is drilled with a series of small diameter holes oriented at right angles to the direction of gas flow. The whole rake assembly can be moved back and forth along the direction of gas flow so that the optical properties along the length of the reaction flame can be examined by moving the rake assembly relative to the fixed optical system. This design is an adaptation of a laser described earlier by Hinchey and Banas (52). The

III. FUTURE PLANNING

Although this AFOSR program is ended, the interest and work in cryochemical lasing is continuing unabated. Exploratory work with unusual species to chemically pump high powered visible and infrared lasers remains a major motivation, and these efforts are continuing in exactly the same guises as described in the preceding pages of this report.

A new interest is developing in this laboratory in bond specific photochemistry using tunable dye lasers. By depositing energy in exactly the critical place in a reactant molecule, one has the opportunity to guide the course of the subsequent reaction. Greatly enhanced yields due to this specificity are possible, and thus the ancient nemesis of undesirable side reactions and competing reactions in chemical processing may be overcome. In contrast to such specific stimulation of reactions, merely heating a reaction mass produces broad and general stimulation of all possible reactions. But until now, this has been the only technique economically at the disposal of the chemical engineer.

This sharpening of focus that the dye laser permits is sure to have far-reaching implications in industrial chemistry. One of the most talked about applications of this new art is in isotope separation, particularly U^{235} and U^{238} and Li^6 and Li^7 . This application is somewhat spectacular because of the implications in fission and fusion power respectively, but many other significant problems are amenable to such an approach.

We will keep AFOSR advised of progress in each of these areas as it develops.

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Appendix A

Personnel

Appendix A

Personnel

The individuals who have contributed to this program are as follows:

- a) Dr. Cathy N. Cardwell who earned her Ph.D. in Physical Chemistry from the University of Rochester in 1972 with thesis research in kinetics and mechanisms of inorganic reactions.
- b) Dr. Edward S. Gregorek, Jr., who received his Ph.D. in Chemistry from Lehigh University in 1967, and who has also worked at Penn State University.
- c) Mr. (Mike) Ngoc LeSi, a native of Saigon, Viet Nam who earned his B.S. in Chemical Engineering from the University of Tennessee in 1967. His work in submerged combustion at cryogenic temperatures in this AFOSR program formed his thesis and for which he received the M.S. degree in Chemical Engineering in August 1974.
- d) Dr. Jay E. Field who earned his Ph.D. in physical chemistry from the University of Florida with expertise in molecular beam scattering and spectroscopy.
- e) Mr. James Allen Foster who was a summer research student and a rising senior working toward his B.S. in Chemistry from Madison College. He was concerned with developing a reactor configuration for the production of oxygen from H_2O_2 and CaF_2 .

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Electric discharge and pyrolytic activation combined with cryogenic quenching have been utilized to synthesize isolable quantities of unusual small compounds of the first row elements. Most are endothermic and stable only at low temperatures. Several of these species have been burned in laser cavities of several designs to explore their efficacy in producing population inversions. Results have been generally disappointing, for no new lasers have been discovered, but work is continuing.		